PHOTOCATALYSED DEGRADATION OF FEW SELECTED ORGANIC SYSTEMS IN AQUEOUS SUSPENSION OF SEMICONDUCTOR

ABSTRACT
THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

CHEMISTRY

By

MALIK MOHIBBUL HAQUE

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

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ABSTRACT

The toxic organic substances are introduced into the water systems through various sources such as industrial effluents, agricultural runoff and chemical spills. The removal of organic pollutants from water is an important measure in environmental protection. Development of appropriate methods for the purification of contaminated drinking, ground and surface water, containing toxic or nonbiodegradable compounds is necessary. Among many processes proposed and/or being developed for the destruction of the organic contaminants, biodegradation has received the greatest attention. However, many organic chemicals, especially which are toxic or refractory, are not amendable to microbial degradation. The incapability of conventional wastewater treatment methods to effectively remove many biorecalcitrant pollutants evidences that new efficient treatment methods are needed. During the past two decades, the photocatalytic process involving TiO_2 semiconductor particles under UV light irradiation has been shown to be potentially advantageous and useful in the treatment of wastewater pollutants. The photocatalyst on excitation generates (e^- / h^+) pair with free electrons produced in the nearly empty conduction band leaving the +ve hole in the valence band. These electron and hole are capable of initiating a series of chemical reactions that eventually can mineralize the organic compounds. More over the formation

of harmless end product represents another attractive feature of this process.

This thesis deals with the photocatalytic degradation of few selected organic pollutants in aqueous system of titanium dioxide under a variety of conditions with an aim to determine the optimal degradation condition and also to identify the intermediate products formed during the photooxidation process through GC/MS analysis technique.

The thesis entitled ***"Photocatalysed degradation of few selected organic systems in aqueous suspension of semiconductor"*** is divided into four chapters.

The Chapter 1 of the thesis deals with the photocatalysed degradation of three selected pesticide derivatives such as isoproturon (**1**), chlorotoluron (**2**) and chlorbromuron (**3**) in aqueous suspensions of titanium dioxide in the presence of light and oxygen. The degradation was studied under a variety of conditions such as type of photocatalyst, pH, substrate and catalyst concentration and in the presence of different electron acceptors in addition of molecular oxygen. The irradiation experiments were carried out using the "Pyrex" filtered out put of a 125 W medium pressure mercury lamp in an immersion well photochemical reaction vessel. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique

and decrease in Total Organic Carbon (TOC) content as a function of irradiation time. The degradation of the pesticide derivative **1** was also investigated under sunlight and efficiency of degradation was compared with that of the artificial light source.

The degradation rates for the decomposition (change in absorption intensity Vs irradiation time) and mineralization (depletion in TOC Vs irradiation time) of the pollutants was determined from the linear regression of plot of the natural logarithm of TOC and the model pollutant concentration as a function of irradiation time. i.e. first order kinetics. The rate was calculated in terms of *mole* L^{-1} *min*$^{-1}$ employing the following equations;

$$\frac{-d[TOC]}{dt} = kc^{n}$$

$$\frac{-d[A]}{dt} = kc^{n}$$

TOC = Total Organic Carbon, A = absorbance, k = rate constant, c = concentration of pollutant, n = order of reaction.

The degradation rates were found to be strongly influenced by all the parameters studied.

An attempt was made to identify the intermediate products formed during the photooxidation process of the pesticide derivative under investigations through GC/MS analysis technique. The products were

characterized based on their molecular ion and mass spectrometric fragmentation pattern. Irradiation of an aqueous solution (250 mL) of isoproturon (**1**, 0.3 mM) in the presence of TiO_2 (1.5 gL^{-1}) for 2 h, followed by GC/MS analysis of the methylene chloride extract gave 4-isopropyl-phenylurea (**10**), 4-isopropylaniline (**11**) and 1,1-dimethyl-3-phenylurea (**9**) as the identified degradation product along with some unchanged starting material. The irradiation of an aqueous solution of chlorotoluron (**2**, 0.35 mM, 250 ml) under analogous conditions gave 3-(3-hydroxy-4-methyl-phenyl)-1,1-dimethyl-urea (**17**), (3-chloro-4-methyl-phenyl) urea (**18**) and 3-chloro-4-methyl-phenylamine (**19**) along with some unchanged starting material.

The Chapter 2 of the thesis deals with the photocatalysed degradation of four selected pesticide derivatives such as, thiram (**1**), carbaryl (**2**), zineb (**3**) and sodium diethyldithiocarbamate (**4**) in aqueous suspensions of titanium dioxide using different parameters. The decomposition and mineralization of the pesticides were monitored by measuring the change in substrate concentration and depletion in TOC content as a function of irradiation time. The degradation rate for the decomposition and mineralization of the pollutant was found to be strongly influenced by all the parameters studied such as type of photocatalyst, pH,

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The Chapter 3 of the thesis deals with the photocatalysed degradation of two selected surfactant, N,N-bis(2-hydroxyethyl)dodecanoyl amide (**1**), cetyl trimethyl ammoniumbromide (**2**) and a textile dye derivative, bromothymol blue (**3**) in aqueous suspensions of titanium dioxide under varying conditions. As usual the decomposition and mineralization was studied UV spectroscopically and using TOC analyzer. The photocatalyst, Degussa P25 was found to be more efficient for the degradation of these pollutants. The degradation product formed during the photooxidation process of the surfactant **1**, in the presence of Degussa P25 was analyzed through GC/MS analysis technique. A probable pathway for the decomposition of surfactant **1** has been proposed.

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Reasonable mechanisms have been suggested to account for the formation of the various products in the reaction of different pollutants listed under Chapters 1-3.

Note: The numbers of the various compounds given in parentheses corresponds to those under the respective chapters.

List of Publications

1. Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspension of titanium dioxide

   M. M. Haque and M. Muneer

   J. Environ. Manag., 69 (**2003**) 169-176.

2. Photocatalytic degradation of a fungicide, thiram in aqueous suspension of titanium dioxide.

   M. M. Haque and M. Muneer

   Ind. J. Chem. Technol., 12 (**2005**) 68-74.

3. Photodegradation of surfactants N,N-bis(2-hydroxyethyl)dodecanoyl amide and cetyl trimethyl ammonium bromide in aqueous suspension of titanium dioxide.

   M. M. Haque and M. Muneer

   Int. J. Photoenergy, (communicated).

4. Titanium dioxide mediated photocatalyzed degradation of three selected pesticide derivatives, carbaryl, zineb and sodium diethyldithiocarbamate in aqueous suspension.

   M. M. Haque and M. Muneer

   Wat. Environ. Manag., (communicated).

5. Semiconductor mediated photocatalysed degradation of a herbicide derivative, chlorotoluron in aqueous suspension.

   M. M. Haque and M. Muneer

   Environ. Toxicol. Chem., (communicated).

6. Photocatalytic degradation of chlorbromuron in aqueous suspension of semiconductor.

   M. M. Haque and M. Muneer

   Asian. J. Environ. Poll., (communicated)

7. TiO_2-mediated photocatalytic degradation of a textile dye derivative, bromothymol blue in aqueous suspension.

   M. M. Haque and M. Muneer

   Dyes and Pigm., (communicated).

8. Photodecomposition of norfloxacin in aqueous suspension of titanium dioxide.

   M. M. Haque and M. Muneer

   Sci. Total Environ., (under preparation).

9. Photodegradation of antibiotics, ciprofloxacin and amoxicillin in aqueous suspension of titanium dioxide.

   M. M. Haque and M. Muneer

   Aquatic Sci., (under preparation).

Paper presented at conference:

Heterogeneous photocatalysed degradation of a herbicide derivatve, isoproturon in aqueous suspension of titanium dioxide under UV light and sunlight.

M. M. Haque and M. Muneer

89th session of Indian Science Congress, Lucknow, India January 3-7 (2002).

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DEDICATED
TO
MY GRANDFATHER
(DADA)

Dr. M. Muneer
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Dated: .....

CERTIFICATE

Certified that the work embodied in this thesis entitled "PHOTOCATALYSED DEGRADATION OF FEW SELECTED ORGANIC SYSTEMS IN AQUEOUS SUSPENSION OF SEMICONDUCTOR" has been carried out by Mr. Malik Mohibbul Haque under my supervision and same has not been submitted elsewhere for a degree.

M. Muneer

(M. MUNEER)
Supervisor

CONTENTS

STATEMENT

I hereby declared that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Aligarh Muslim University, Aligarh, India, under the supervision of Dr. M. Muneer.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Malik - Mohibbul Haque

(**MALIK MOHIBBUL HAQUE**)

ACKNOWLEDGEMENT

It is with great pleasure that I express my deep sense of gratitude to my supervisor, Dr. M. Muneer, for suggesting the research problem and for encouraging me to a successful completion of this work.

I am highly obliged to Prof. Kabiruddin, Chairman, Department of Chemistry, Aligarh Muslim University, Aligarh for providing me necessary facilities and their kind support through out the period of endeavor to Ph.D. study. I am also thankful to all teaching and non-teaching staff of Department of Chemistry, AMU, Aligarh for their cooperation especially to Mr. Aurangzeb, Micro Analyst, for providing me the instrumentation facilities.

I am immensely thankful to all my friends and my colleagues Messrs M. A. Rahman, H. K. Singh, M. Qamar, M. A. Tariq, M. Faisal and Dr. M. Saquib, whose guidance and cooperation at every stage has, enable me to complete this work successfully and efficiently.

I express my deepest appreciations to my parents, sisters, brothers in law, nieces and nephew for their untiring assistance, constant encouragement and full cooperation throughout the tenure of this work.

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Malik-Mohibbul Haque

(**Malik Mohibbul Haque**)

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Reasonable mechanisms have been suggested to account for the formation of the various products in the reaction of different pollutants listed under Chapters 1-3.

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Chapter 1

PHOTOCATALYSED DEGRADATION OF THREE SELECTED UREA DERIVATIVE PESTICIDES, ISOPROTURON, CHLOROTOLURON AND CHLORBROMURON IN AQUEOUS SUSPENSION OF SEMICONDUCTOR[1-3]

1.1 Abstract

The photocatalysed degradation of three selected urea derivative pesticide, such as isoproturon (**1**), chlorotoluron (**2**) and chlorbromuron (**3**) have been investigated in aqueous suspensions of titanium dioxide (TiO_2) under a variety of conditions. The degradation has been studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique and decrease in Total Organic Carbon (TOC) content as a function of irradiation time. The degradation of the pesticide was studied under different conditions such as different types of TiO_2, pH, catalyst concentration, substrate concentration, and in the presence of electron acceptors besides molecular oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The degradation of isoproturon (**1**) was also investigated

under sunlight and the efficiency of degradation was compared with that of the artificial light source. The photocatalyst Degussa P25 was found to be more efficient for the degradation of all the pesticides under investigation. The degradation products were analyzed by GC/MS analysis technique and probable pathways for the formation of different products have been proposed.

1.2 Introduction

Total amount of water existing on earth is around 1.4×10^9 km^3 from where only ~0.8 – 1.0% (i.e., ~1.3×10^7 km^3) corresponds to total drinking water.[4] The water present on earth (ground water, surface water) is contaminated through various sources such as industrial effluents, agricultural runoff and chemical spills[5]. The total amount of water used for drinking purpose per year is between 10 and 30×10^3 km^3.[6] This shows that even a small shortage of water can become a threat to mankind especially in developing countries where a high percentage of diseases are caused by a deficient water supply or by the supply of the contaminated water. This number is in crisis due to the development of a consumer society that entails the augmentation of industrial or agro-industrial activities. Hence, their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to the societies and regulation authorities around the world.[7] For this

reason strategies should be made for water treatment in order to counterbalance these growing environmental problems.

The control of organic pollutants in water is an important measure in environmental protection. Development of appropriate methods for the degradation of contaminated drinking, ground, surface waters, wastewaters containing toxic or nonbiodegradable compounds is necessary. Among many processes proposed and/or being developed for the destruction of the organic contaminants, biodegradation has received the greatest attention. However, many organic chemicals, especially which are toxic or refractory, are not amendable to microbial degradation. The incapability of conventional wastewater treatment methods to effectively remove many biorecalcitrant pollutants evidences that new efficient treatment systems are needed. Besides biological processes, several oxidation systems are currently used and some are in different stages of development. For the last 25 years the water purification research has been extensively growing. Rigorous pollution control and legislation in many countries have resulted in an intensive search for new and more efficient water treatment technologies.

During the past two decades, photocatalytic processes involving TiO_2 semiconductor particles under UV light illumination have been shown to be potentially advantageous and useful in the treatment of wastewater

pollutants. Earlier studies[8–12] have shown that a wide range of organic substrates such as alkanes, alkenes, aromatics, surfactants, herbicides, pesticides, fungicides and insecticides can be completely photomineralized in the presence of TiO_2 and oxygen.

1.2.1 Mechanism of heterogeneous photocatalysis

Heterogeneous photocatalysis is a process in which two active phases solid and liquid are present. The solid phase is a catalyst, usually a semiconductor. The molecular orbitals of semiconductors have a band structure. The bands of interest in photocatalysis are the populated valence band (VB) and its largely vacant conduction band (CB),[13] which is commonly characterized by band gap energy (E_{bg}). The semiconductors may be photoexcited to form electron-donor sites (reducing sites) and electron-acceptor sites (oxidising sites), providing great scope for redox reaction. When the semiconductor is illuminated with light ($h\nu$) of greater energy than that of the band gap, an electron is promoted from the VB to the CB leaving a positive hole in the valence band and an electron in the conduction band as illustrated in Fig. **1.1**.

If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h^+_{vb} may react with surface-bound H_2O or $^{\bullet}OH$ to produce the hydroxyl radical and e^-_{cb} is picked up by oxygen to

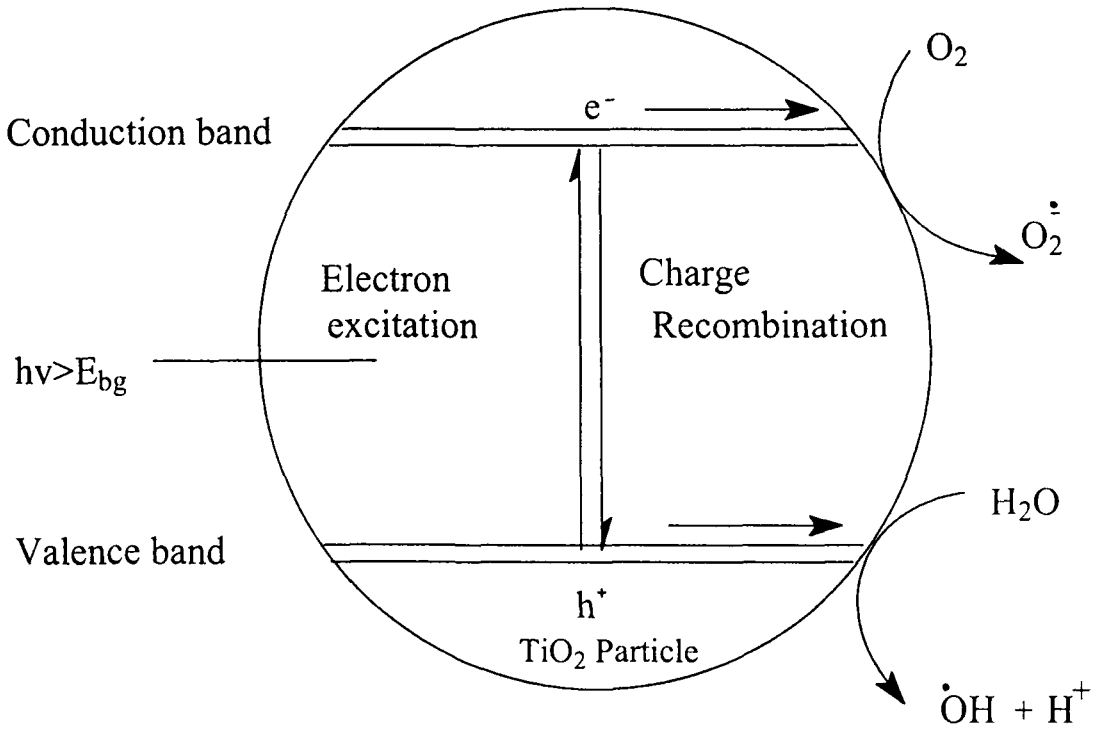

Conduction band
e⁻
O2
O2·-
Electron
excitation
Charge
Recombination
hv>Ebg
H2O
Valence band
h+
TiO2 Particle
·OH + H+

Figure 1.1

generate superoxide radical anion ($O_2^{\bullet-}$), as indicated in the following equation 1-3;

$$TiO_2 + hv \rightarrow e^-_{cb} + h^+_{vb} \quad [1]$$

$$O_2 + e^-_{cb} \rightarrow O^{\bullet-}_2 \quad [2]$$

$$H_2O + h^+_{vb} \rightarrow {}^{\bullet}OH + H^+ \quad [3]$$

It has been suggested that the hydroxyl radicals ($^{\bullet}OH$) and superoxide radical anions ($O_2^{\bullet-}$) are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would results in the degradation of the pollutants.

For oxidation reactions to occur, the VB must have a higher oxidation potential than the material under consideration. The redox potential of the VB and the CB for different semiconductors varies between +4.0 and -1.5 volts versus Normal Hydrogen Electrode (NHE) respectively. Therefore, by careful selection of the semiconductor photocatalyst, a wide range of species can be treated via these processes.

Among the semiconductors, TiO_2 has proven to be the most suitable for widespread environmental applications. Titanium dioxide is biologically and chemically inert; it is stable to photo- and chemical corrosion, and inexpensive. It also shows the resistivity against strong acids and bases

and its stability under illumination.[14] Furthermore, TiO_2 is of special interest since it can use natural (solar) UV radiation. This is because TiO_2 has an appropriate energetic separation between its valence and conduction bands, which can be surpassed by the energy of a solar photon. The VB and CB energies of the TiO_2 are estimated to be +3.1 and -0.1 volts, respectively, which means that its band gap energy is 3.2 eV and therefore absorbs in the near UV light (λ<387 nm). Many organic compounds have a potential above that of the TiO_2 valence band and therefore can be oxidized. In contrast, fewer organic compounds can be reduced since a smaller number of them have a potential below that of the TiO_2 conduction band.[15] Although ZnO seems to be a suitable alternative to TiO_2, it dissolves in acidic solutions and can therefore not be used for technical applications.[16] Other semiconductor particles (e.g., CdS or GaP) absorb larger fractions of the solar spectrum than TiO_2 and can form chemically activated surface-bond intermediates, but unfortunately, such catalysts are degraded during the repeated catalytic cycles usually involved in heterogeneous photocatalysis.

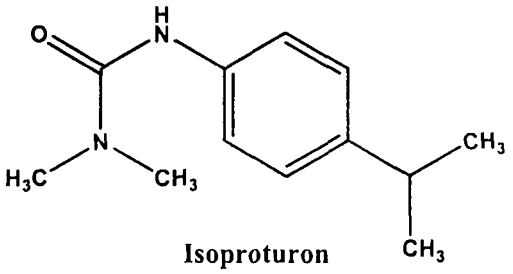
A large amount of chemicals are used in agricultural field for better quality and quantity of the crop. These compounds due to chemical resistivity, resistance to biodegradation and with sufficient water solubility penetrate deep into the ground water leading to surface and underground

water contamination. These contaminated water should be purified before it is used for any other purpose.

In the first chapter of the thesis, we have studied few selective urea derivative, which are used as herbicides throughout the world with very similar molecular structures acting by inhibition of photosynthesis to regulate the plant growth.[17] These are used for pre- and post-emergence control of annual grass, wild oats, annual meadow grass and many broad leaf weeds in winter wheat, spring and winter barley and winter rye.[18] The presence of herbicides in ground waters, surface waters, effluents of wastewater treatment plants, and other sources of drinking water, indicates that many of these compounds are recalcitrant and/or non-biodegradable. It can also persist for long periods in the environment. Several studies have been reported earlier on the direct phototransformation of isoproturon.[19-21] Dureja et al., identified a number of photoproducts on irradiating an aqueous solution using 254 and 360 nm light source.[20] The integrated photocatalytic-biological flow system using supported TiO_2 and fixed bacteria for the mineralization of isoproturon has been recently studied.[22] Degradation[23] and phototransformation[19] of chlorotoluron have been reported earlier.

In spite of these studies, no major efforts have been made to look into the detailed degradation kinetics and identification of intermediate

products formed during the photooxidation process. With this view, we have studied the degradation of three selected pesticide derivatives such as isoproturon (**1**), chlorotoluron (**2**) and chlorbromuron (**3**) shown in Chart **1.1**, in aqueous suspensions of TiO_2 under a variety of conditions and attempt has been made to identify the intermediate products formed during the photooxidation process through GC/MS analysis technique.

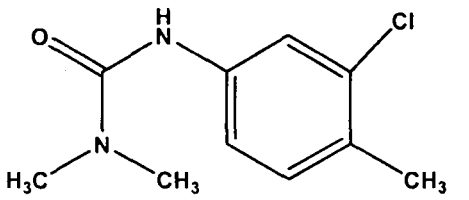


Isoproturon

N-(4-isopropylphenyl)-N',N'-dimethylurea

$C_{12}H_{18}N_2O$

1

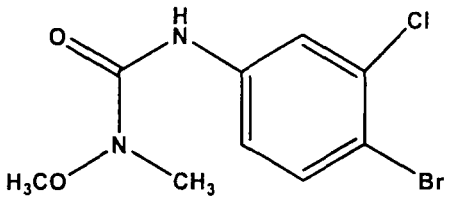


Chlorotoluron

3-(3-chloro-p-tolyl)-1,1-dimethylurea

$C_{10}H_{13}ClN_2O$

2



Chlorbromuron

3-(4-Bromo-3-chloro-phenyl)-1,1-dimethyl-urea

$C_9H_{10}BrClN_2O_2$

3

Chart 1.1 Chemical structure, common name, chemical name and chemical formula.

1.3 Experimental

1.3.1 Reagent and chemicals

Laboratory grade isoproturon (**1**) obtained from Motilal Pesticides, Mathura, India was used for kinetic study whereas analytical grade otained from Fluka was used for intermediate study. Chlorbromuron (**3**) was purchased from Aldrich and used as such without any further purification. The urea derivative chlorotoluron (**2**) was a gift sample from Prof. P. Boule.[24] The water employed in all the studies was double distilled. The photocatalyst titanium dioxide, Degussa P25 (Degussa AG),[25] was used in most of the experiments, whereas other catalyst powders namely Hombikat UV100 (Sachtleben chemie GmbH),[26] PC500 (Milenium inorganic chemicals),[26] and TTP (Travancore titanium products, India)[27]. Degussa P25 consist of 75% anatase and 25% rutile with a specific BET-surface area of 50 m^2g^{-1} and primary particle size of 20 nm.[28] Hombikat UV100 consist of 100% anatase with a specific BET-surface area >250 m^2g^{-1} and primary particle size of 5 nm.[29] The photocatalyst PC500 has a BET-surface area of 287 m^2g^{-1} with 100% anatase and primary particle size of 5-10 nm,[30] whereas, TTP has a BET-surface area of 9.82 m^2g^{-1}. The other chemical used in this study such as NaOH, HNO_3, $K_2S_2O_8$, H_2O_2 and $KBrO_3$ were obtained from Merck.

1.3.2 Procedure

Stock solutions of the pesticide containing the desired concentration were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, water circulating jacket and an opening for supply of molecular oxygen was used. A simplified diagram of the reactor system is shown in Fig. **1.2**.

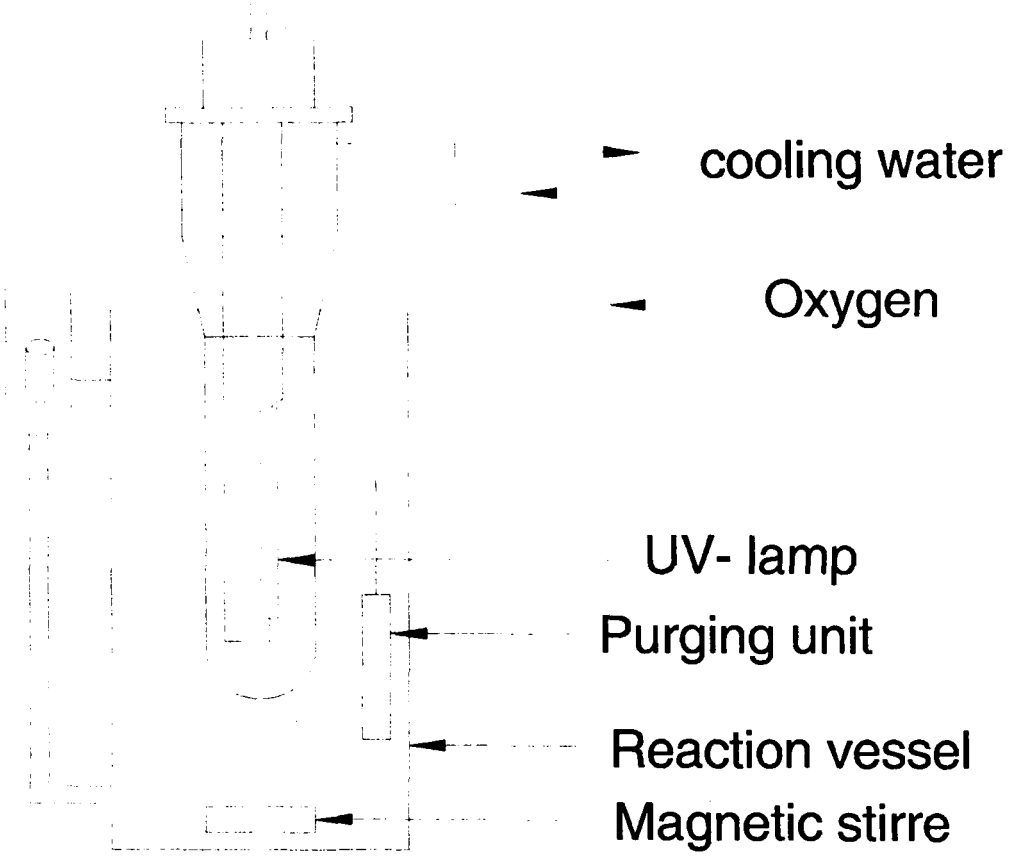


Figure 1.2

For irradiation experiment the aqueous solution of the pesticide with desired concentration was taken into the photoreactor and required amount of photocatalyst was added. Then solution was stirred and bubbled with molecular oxygen for at least 15 minutes in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (Philips). IR-radiation and short-wavelength UV-radiation were eliminated by water circulating Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during irradiation and analyzed after centrifugation.

The sunlight experiments were carried out between 9:00 A.M to 2:30 P.M during the month of November at Aligarh City which is about 140 Km from New Delhi. Reactions were carried out in a round bottom flask made of Pyrex glass. Aqueous solution (250 mL) of desired concentration of the model compound containing required amount of photocatalyst was taken and stirred for 15 min in the dark in presence of oxygen for equilibration. The solution was then placed on flat platform under sunlight with continuous stirring and purging of molecular oxygen. Samples (10 mL)

were collected before and at regular intervals during the illumination and analyzed after centrifugation.

1.3.3 Analysis

1.3.3.1 Photomineralization of the pesticide

The photomineralization of the pesticide was measured using Total Organic Carbon analyzer (Shimadzu TOC 5000 A).[31] The main principle of TOC analyzer involves the use of carrier gas (oxygen), which is flow-regulated (150 ml / min) and allows to flow through the total carbon (TC) combustion tube, which is packed with catalyst, and kept at 680 ^{0}C. When the sample enters the TC combustion tube, TC in the sample is oxidized to carbon dioxide. The carrier gas containing the combustion products from the TC combustion tube flows through the inorganic carbon (IC) reaction vessel, dehumidifier, halogen scrubber and finally reaches the sample cell of the nondispersive infrared (NDIR) detector which measures the carbon dioxide content. The output signal (analog) of the NDIR detector is displayed as peaks. The peak areas are measured and processed by the data processing unit. Since the peak areas are proportional to the total carbon concentration, the total carbon in a sample may be easily determined from the calibration curve prepared using standard solution of known carbon content. Total carbon is the sum of TOC (Total Organic Carbon) and IC (Inorganic Carbon).

1.3.3.2 Photodegradation of the pesticide

The photodegradation of the pesticide was measured using UV spectroscopic analysis technique (Shimadzu UV-Vis 1601). The double beam spectrophotometer has an in-built tungsten and deuterium lamps, which provide the measurement of optical density (OD) in the range 200-1100 nm (near UV and visible regions). The samples were analyzed using quartz cuvette, as it has zero absorption in the above wavelength regions.

The absorbance of the pesticide derivative isoproturon (**1**), chlorotoluron (**2**) and chlorbromuron (**3**) were followed at 238 nm (after 75% dilution), 242 and 246 nm, respectively.

1.3.3.3 Characterization of intermediate products[32]

For the characterization of intermediate products, aqueous solutions (250 mL) of the pesticide containing TiO_2 (P25, 1 gL^{-1}) were taken in a photochemical reactor made of Duran glass with a plain quartz window (through which the parallel light beam is entering) equipped with a magnetic stirring bar, a water-circulating jacket and opening for electrodes and gas supplies. Irradiations were carried out using a high pressure mercury lamp (Osram HBO 450 w). The light intensity was found to be 20 mW/cm^2. IR radiation and short-wavelength UV radiation were eliminated by a 10 cm water filter. A 320 nm cut-off filter was used to avoid any direct

excitation of the compound under investigation. Sample were collected at different time intervals during the irradiation, centrifuged to remove TiO_2 and extracted with methylene chloride, which was subsequently dried over anhydrous sodium sulphate and analyzed by GC/MS. For GC/MS analysis a Shimadzu Gas Chromatograph and Mass Spectrometer (GCMS-QP 5050) equipped with a 25m CP SIL 19 CB (d=0.25mm) capillary column, operating temperature programmed (220^0C for 40 min at the rate of 10^0C min^{-1}) in splitless mode injection volume (1.0 μL) with helium as a carrier gas was used.

1.4 Results and Discussion

1.4.1 Photolysis of aqueous suspension of pesticide derivative (1-3) in the presence of TiO_2

Irradiation of an aqueous suspension of the pesticide derivative under investigation in the presence of TiO_2 lead to decrease in absorption intensity and depletion in TOC content as a function of time.

Figs. **1.3** and **1.4** show the change in absorption intensity and depletion in TOC as a function of time on irradiation of an aqueous solution of isoproturon (**1**, 0.5 mM) and chlorotoluron (**2**, 0.25 mM), respectively, in the presence and absence of the photocatalyst (Degussa P25, 1 gL^{-1}) by

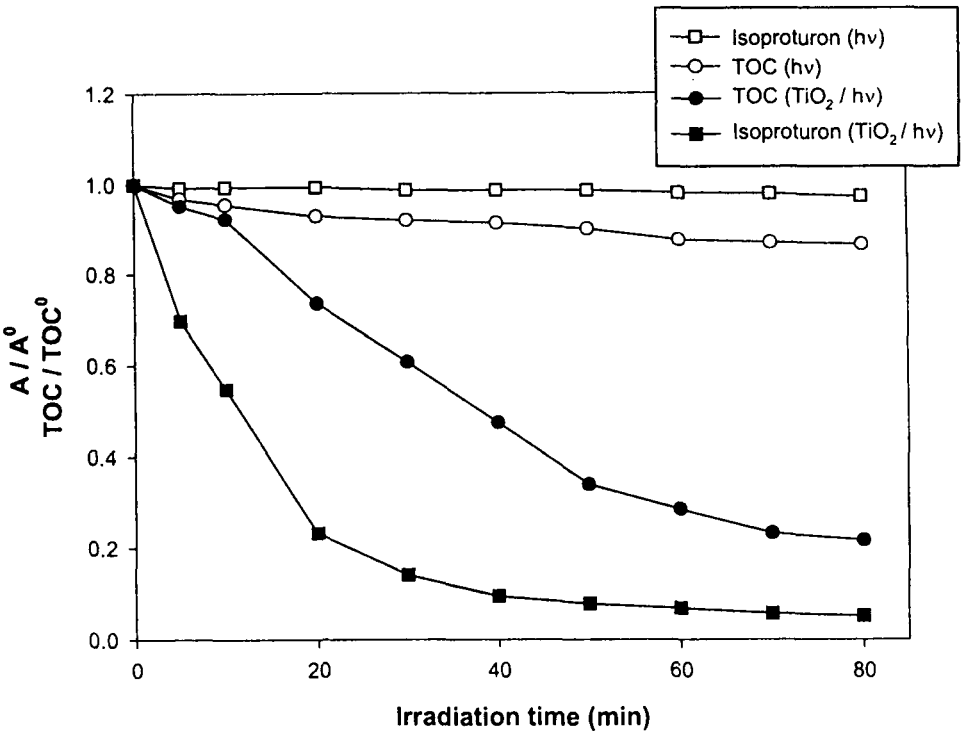


Figure 1.3. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of isoproturon (**1**) in the presence and absence of the photocatalyst.

Experimental conditions: 0.5 mM isoproturon, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 238 nm after 75% dilution, cont. O_2 purging and stirring, irradiation time = 80 min.

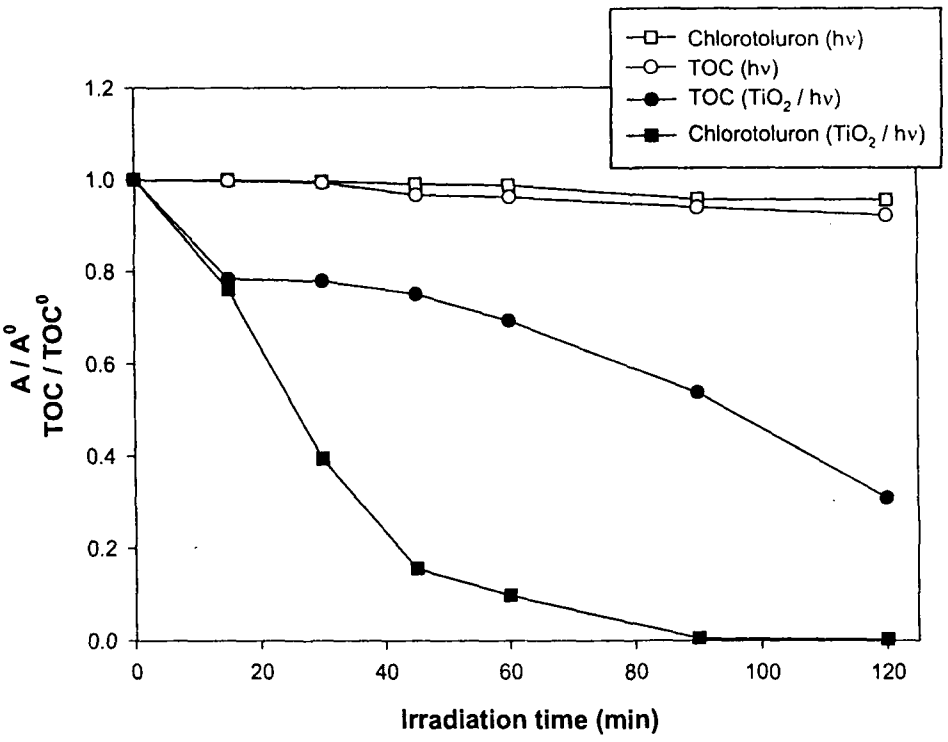


Figure 1.4. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of chlorotoluron (**2**) in the presence and absence of the photocatalyst.

Experimental conditions: 0.25 mM chlorotoluron, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 242 nm, cont. O_2 purging and stirring, irradiation time = 120 min.

the "Pyrex" filtered output of a 125 W medium Pressure mercury lamp. Fig. **1.5** shows the change in absorption intensity at 246 nm on irradiation of aqueous suspension of chlorbromuron (**3**, 0.25 mM) under analogous condition.

Blank experiments were carried out by irradiating the aqueous solution of the pesticides in the absence of TiO_2, where no observable loss of the pesticide was seen. The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

Both the mineralization (depletion of TOC Vs irradiation time) and decomposition (decrease in absorption intensity Vs irradiation time) curves for compounds under investigation can be fitted reasonably well by an exponential decay curve suggesting first order kinetics. As a representative example, Figs. **1.6** and **1.7** show the linear regression curve fit for the natural logarithm of the absorbance and TOC content Vs irradiation time, respectively, for isoproturon (**1**). For each experiment, the degradation rate constant of the pesticide was calculated from the plot of the natural logarithm of the TOC content or absorbance of the pesticide as a function of irradiation time. The degradation rate for the mineralization and for the decomposition of the pesticide was calculated using formula given below;

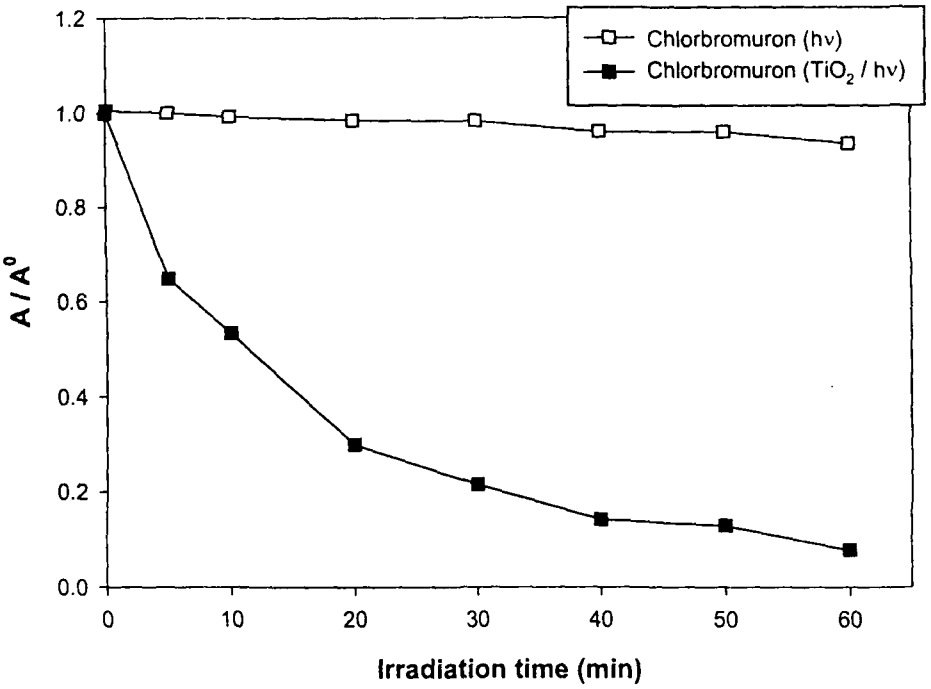


Figure 1.5. Change in absorption intensity at 246 nm as a function of irradiation time for an aqueous solution of chlorbromuron (3) in the presence and absence of the photocatalyst.

Experimental conditions: 0.25 mM chlorbromuron, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 60 min.

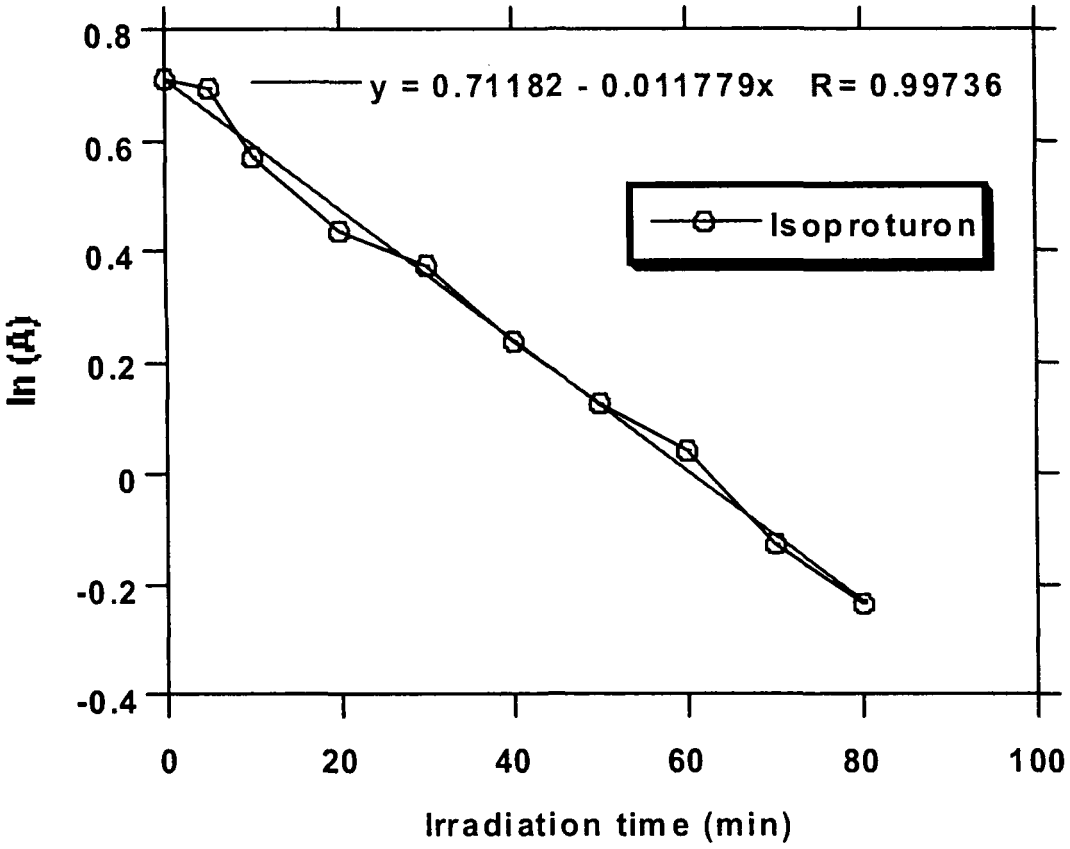


Figure 1.6. Plot showing the linear regression curve fit for the natural logarithm of absorbance of the pesticide concentration of isoproturon (1) against irradiation time.

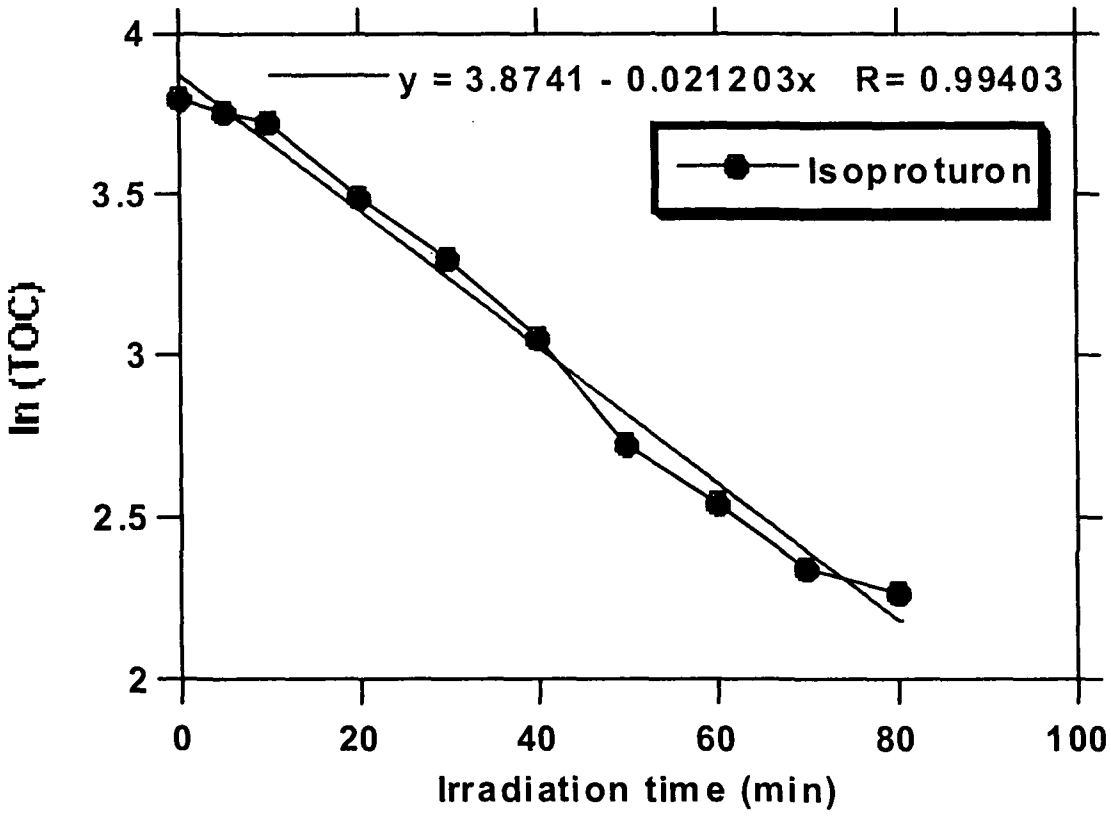


Figure 1.7. Plot showing the linear regression curve fit for the natural logarithm of TOC of isoproturon (**1**) against irradiation time.

$$\frac{-d[TOC]}{dt} = kc^{n} \qquad [4]$$

$$\frac{-d[A]}{dt} = kc^{n} \qquad [5]$$

TOC = Total Organic Carbon, A = absorbance, k = rate constant, c = concentration of the pollutant, n = order of reaction.

The degradation rate for the decomposition and for the mineralization of the pesticide for the first order reaction was calculated in terms of mol L^{-1} min^{-1}.

1.4.2 Comparison of the photocatalytic degradability of the pesticide derivatives (1-3)

Fig **1.8** shows the comparison of degradation rate for the three different pesticide derivatives **1-3**, irradiated with a 125 W medium pressure mercury lamp for 60 min with an initial concentration of 0.25 mM and 1.0 g L^{-1} of TiO_2. It has been found that the degradation of isoproturon (**1**) is faster than chlorotoluron (**2**) and chlorbromuron (**3**). The degradation rate of chlorotoluron is slightly higher than chlorbromuron. The photoreactivity of the three pesticides can then be ranked in the following order : Isoproturon > Chlorotoluron ≥ Chlorbromuron.

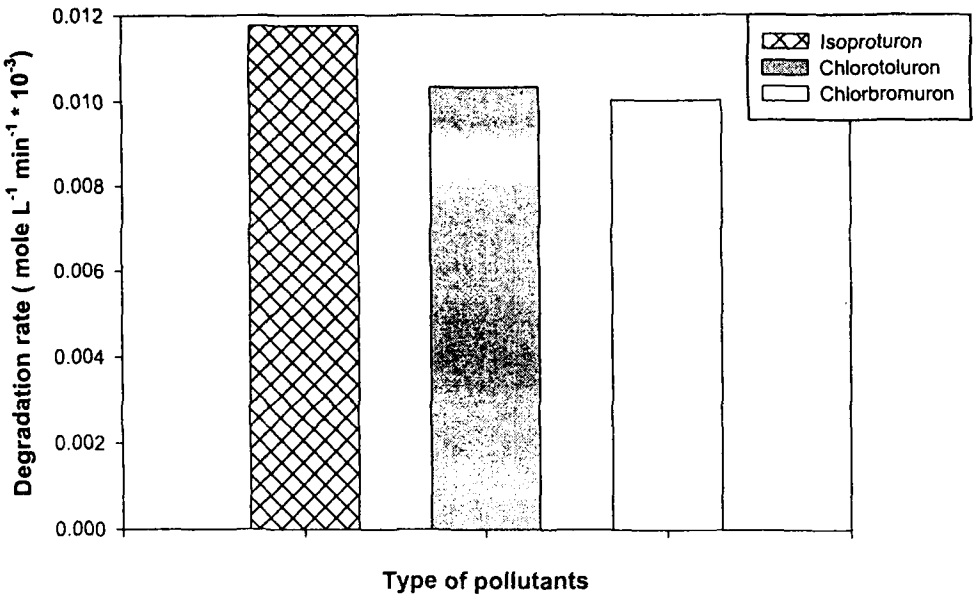
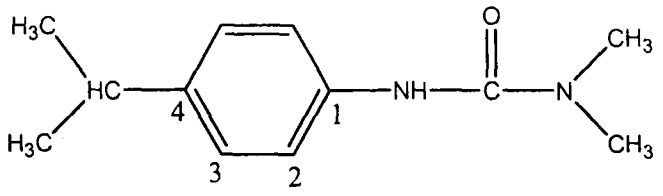


Figure 1.8. Comparison of degradation rate for the decomposition (change in absorption intensity Vs irradiation time) of isoproturon (**1**), chlorotoluron (**2**) and chlorbromuron.

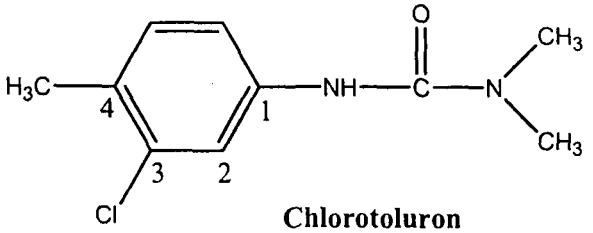
Experimental conditions: pesticide concentration (**1-3**) 0.25 mM, V=250 mL, photocatalyst: TiO_2 Degussa P25 (1 gL^{-1}), light source: 125 W medium pressure mercury lamp, immersion well photochemical reactor, irradiation time = 60 min.

The differences in photoreactivity is directly related to the electron-donor or electron-withdrawing character of the different substituents in the herbicides aromatic ring, which can activate or deactivate the ring with respect to electrophilic attack of the $^{\bullet}OH$ radical. To explain these results, only the effect of substituents in positions 3 and 4 (Chart **1.2**) is taken into account since the substituent in position 1 is similar in all cases.



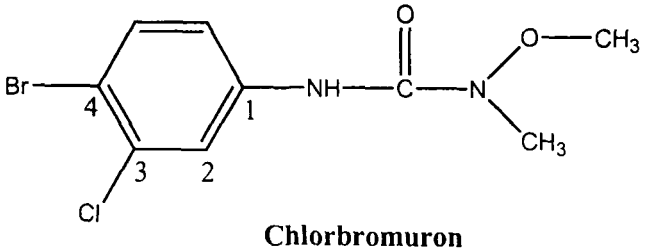
Isoproturon

1



Chlorotoluron

2



Chlorbromuron

3

Chart 1.2

Isoproturon (**1**) has been found to be more reactive substance due to the presence of an activating $CH(CH_3)_2$ at position 4, and absence of an halogen atom on benzene ring. The other two herbicides contain halogen groups that are considered as deactivating. Earlier studies have shown that the degradation rate of chlorophenol decreases with the increase of chlorine group.[33-37] The results obtained in this current work are explained by analogy with this fact. In case of chlorotoluron, it has single halogen groups (Cl) and one CH_3 activating group while in chlorbromuron it has two halogen groups (Cl and Br), bound to the aromatic ring at position 3 and 4. Hence due to the presence of halogen deactivating group it has lower reactivity when compared with the isoproturon. As it is known, the activating character of a CH_3 group prevails over the deactivating character of a Cl group explaining why the degradation rate of chlorotoluron is slightly faster than chlorbromuron.

1.4.3 Comparison of different photocatalysts

Titanium dioxide is known to be the semiconductor with the highest photocatalytic activity, is non-toxic, relatively inexpensive and stable in aqueous solution. Several reviews have been written, regarding the mechanistic and kinetic details as well as the influence of experimental parameters. It has been demonstrated that degradation by photocatalysis can be more efficient than by other wet-oxidation technique.[38]

We have tested the photocatalytic activity of four different commercially available TiO_2 powders (namely Degussa P25, Hombikat UV100, Milenium Inorganic PC500 and Travancore Titanium Product) on the degradation kinetics of the pesticides under investigation. The degradation rate obtained for the decomposition and TOC depletion of **1** and **2**, in the presence of different types of TiO_2 powders is shown in Figs. **1.9-1.10**, respectively. Fig. **1.11** shows the degradation rate for the decomposition of the pesticide derivative **3** in the presence of different TiO_2 powders. It has been observed that the degradation of all the pesticides under investigation proceed much more rapidly in the presence of Degussa P25 as compared with other TiO_2 samples.

The differences in the photocatalytic activity of TiO_2 are likely to be due to differences in the BET-surface, impurities, lattice mismatches or density of hydroxyl groups present on the catalyst's surface. Since they will affect the adsorption behavior of a pollutant or intermediate molecule and the lifetime and recombination rate of electron-hole pairs. Earlier study[39] has shown that Degussa P25 owes its high photoreactivity due to slow recombination between electron and holes whereas Sachtleben Hombikat UV100 has a high photoreactivity due to fast interfacial electron transfer rate. Since the photocatalyst Degussa P25 was found to be more active photocatalyst, it is obvious that the rate-limiting step cannot be interfacial

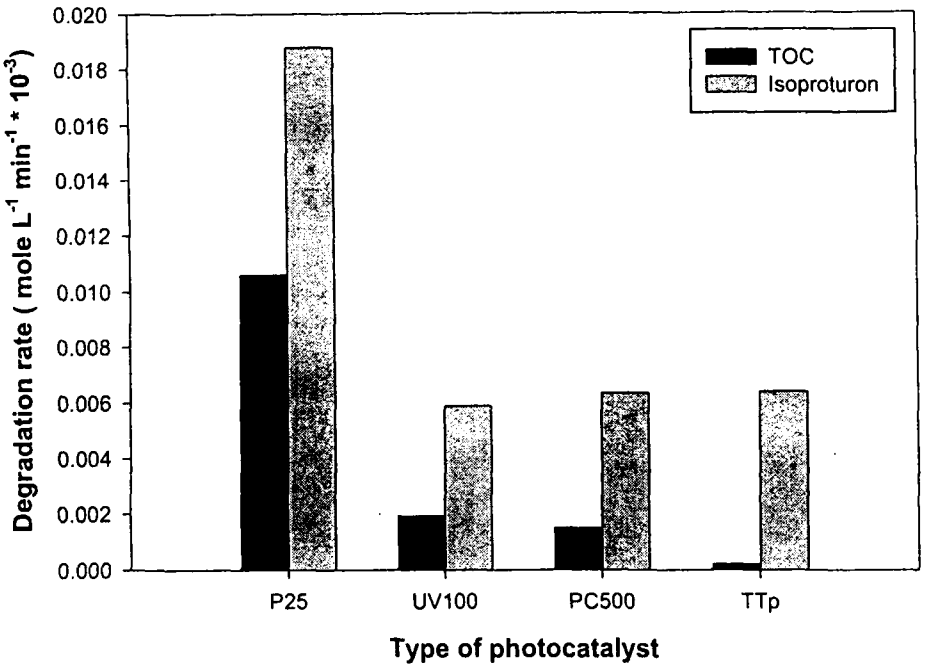


Figure 1.9. Comparison of degradation rate for the mineralization (TOC depletion Vs irradiation time) and for the decomposition (change in absorption intensity Vs irradiation time) of isoproturon (**1**) in the presence of different photocatalysts.

Experimental conditions: 0.5 mM isoproturon, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), TTP (1 gL^{-1}), irradiation time = 80 min.

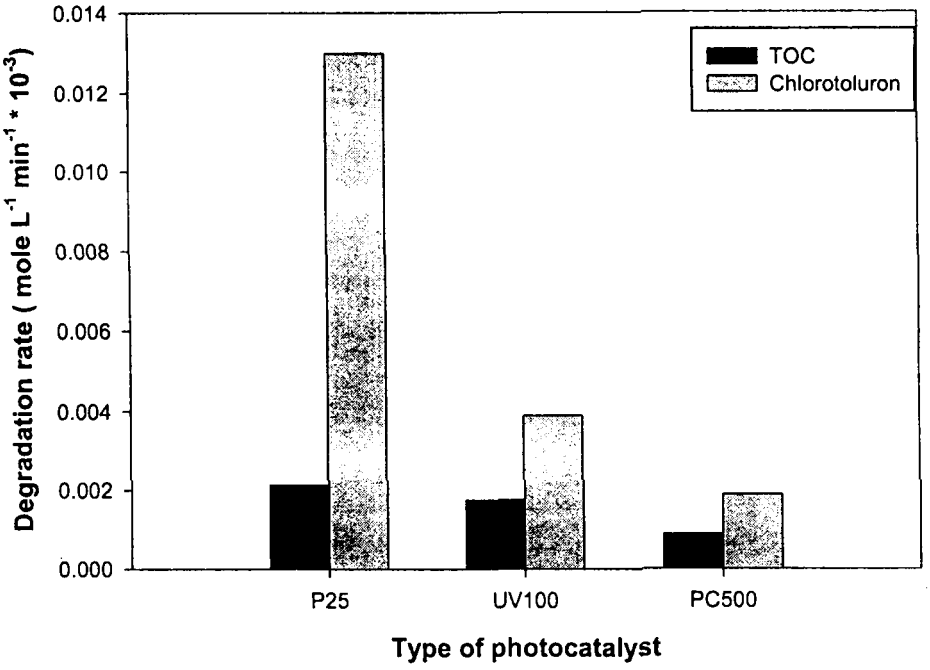


Figure 1.10. Comparison of degradation rate for the mineralization (TOC depletion Vs irradiation time) and for the decomposition (change in absorption intensity Vs irradiation time) of chlorotoluron (**2**) in the presence of different photocatalysts.

Experimental conditions: 0.25 mM chlorotoluron, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), irradiation time = 120 min.

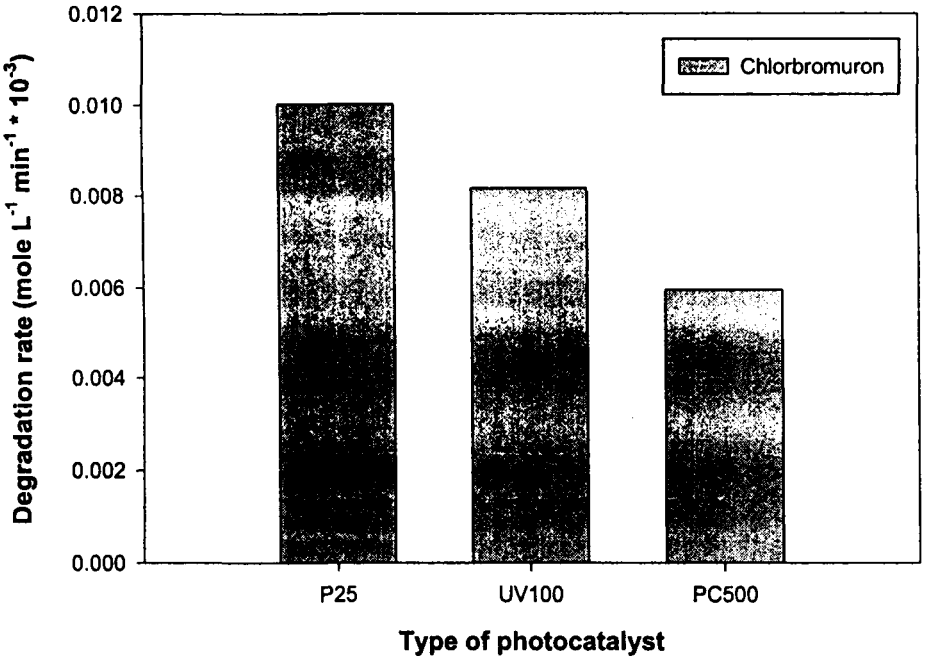


Figure 1.11. Comparison of degradation rate for the decomposition (change in absorption intensity Vs irradiation time) of chlorbromuron (3) in the presence of different photocatalysts.

Experimental conditions: 0.25 mM chlorbromuron, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), irradiation time = 60 min.

electron-transfer rate but rather the lifetime of electron hole pairs. Assuming that the adsorption/desorption of substrate and reaction intermediates is relatively slow in comparison to the recombination rate of electron-hole pair, one should expect higher degradation rates when a photocatalyst such as Degussa P25 is used which guarantees longer lifetime of the electron-hole pairs. Thus, higher concentrations of electrons and holes are available for suitable reactants to initiate the photocatalytic reaction. Earlier studies have shown that Degussa P25 was found to show better activity for the photocatalytic degradation of a large number of organic compounds.[40-42] On the other hand Lindner et al.[43] showed that Hombikat UV100 was almost four times more effective than P25 when dichloroacetic acid was used as the model pollutant. Also Hombikat UV100 was found to be better for the degradation of benzidine, 1,2-diphenyl hydrazine[44] and remazol brilliant blue R[45] as shown in a recent study. These results indicate that the activity of the photocatalyst also depends on the type of the model pollutant.

Another reason for the better photocatalytic activity of Degussa P25, could be attributed to the fact that P25 being composed of small nano-crystallites of rutile being dispersed within an anatase matrix. The smaller band gap of rutile "catches" the photons, generating electron-hole pairs. The electron transfer, from the rutile conduction band to electron traps in

anatase phase takes place. Recombination is thus inhibited allowing the hole to move to the surface of the particle and react.[46] The better efficiency of photocatalyst Degussa P25 may also due to 'quantum size effect'.[47,48] When the particles become too small, there is a 'blue shift' with an increase of the band gap energy, detrimental to the near UV-photon absorption, and an increase of the electron-hole recombination. Too high specific area is not beneficial for an optimum efficiency.

In all following experiments, Degussa P25 was used as the photocatalyst, since this material exhibited the highest overall activity for the degradation of the pesticide.

1.4.4 pH Effect

An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms. Employing Degussa P25 as photocatalyst the decomposition and mineralization of isoproturon (**1**) in the aqueous suspensions of TiO_2 was studied in the pH range between 3-9. Figs. **1.12** and **1.13** show the degradation rate for the TOC depletion and for the decomposition of the pesticide derivatives **1** and **2**, respectively, as a function of pH.

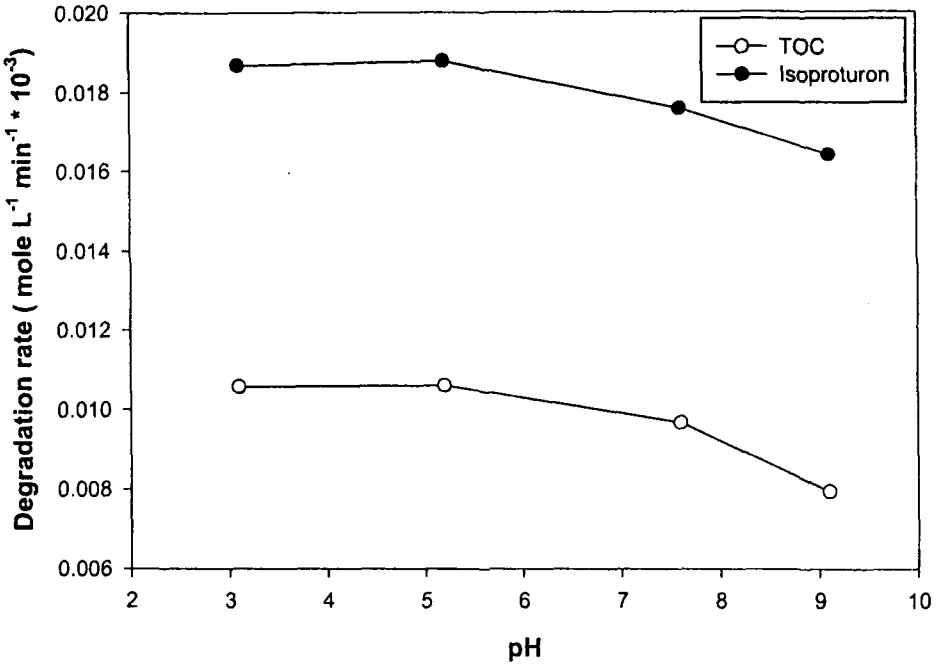


Figure 1.12. Influence of pH on the degradation rate for the mineralization and for the decomposition of isoproturon (1).

Experimental conditions: 0.5 mM isoproturon, V=250 mL, photocatalyst TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (3.1, 5.2, 7.6, and 9.1), irradiation time = 80 min.

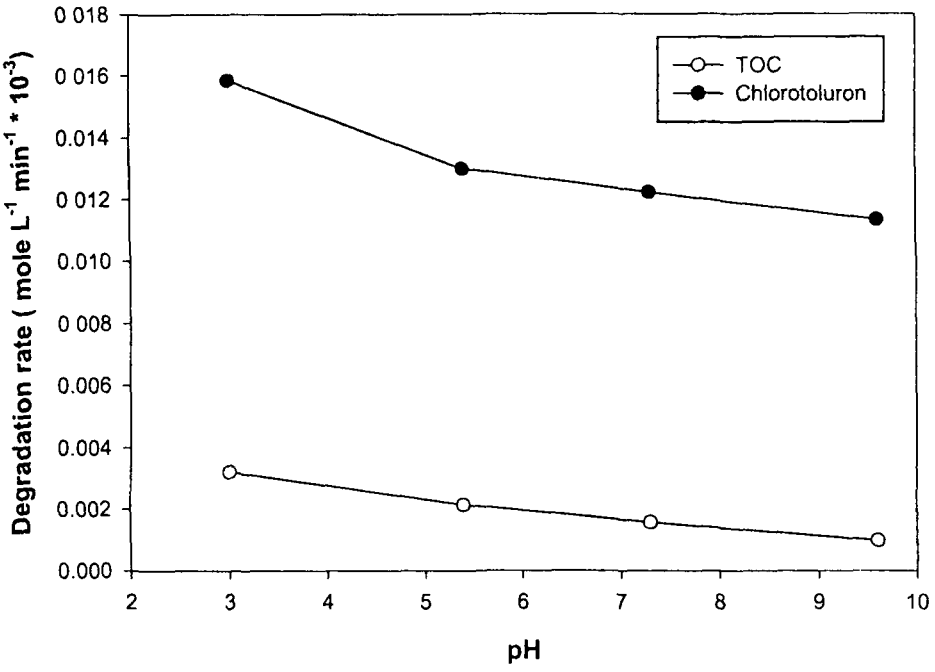


Figure 1.13. Influence of pH on the degradation rate for the mineralization and for the decomposition of chlorotoluron (**2**).

Experimental conditions: 0.25 mM chlorotoluron, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (3.0, 5.4, 7.3, and 9.6, irradiation time = 120 min.

The degradation rate for the decomposition of the pesticide **3**, as a function of reaction pH is shown in Fig. **1.14**. In all the cases it has been observed that the rates were found to be slightly higher under acidic pH, which slowly decreases with increase in pH.

In this study it has been shown that the degradation rate for the TOC depletion and for the decomposition of the pesticide derivatives under investigation is slightly influenced by the reaction pH.

1.4.5 Effect of substrate concentration

It is important both from mechanistic and from application point of view to study the dependence of substrate concentration in the photocatalytic reaction rate. Effect of substrate concentration on the degradation of the pesticide derivatives **1-3** was studied at different concentrations. The degradation rate for the TOC depletion and for the decomposition of **1** and **2** as a function of substrate concentration employing Degussa P25 as photocatalyst is shown in Figs. **1.15**. and **1.16**, respectively. In case of **1** the degradation rate for the decomposition increases with the increase in substrate concentration while the mineralization rate level off as the substrate concentration increases from 0.5 to 0.75 mM. In compound **2** the degradation rate for the decomposition and for the mineralization increases gradually with the increase in substrate concentration from 0.15 to 0.45 mM.

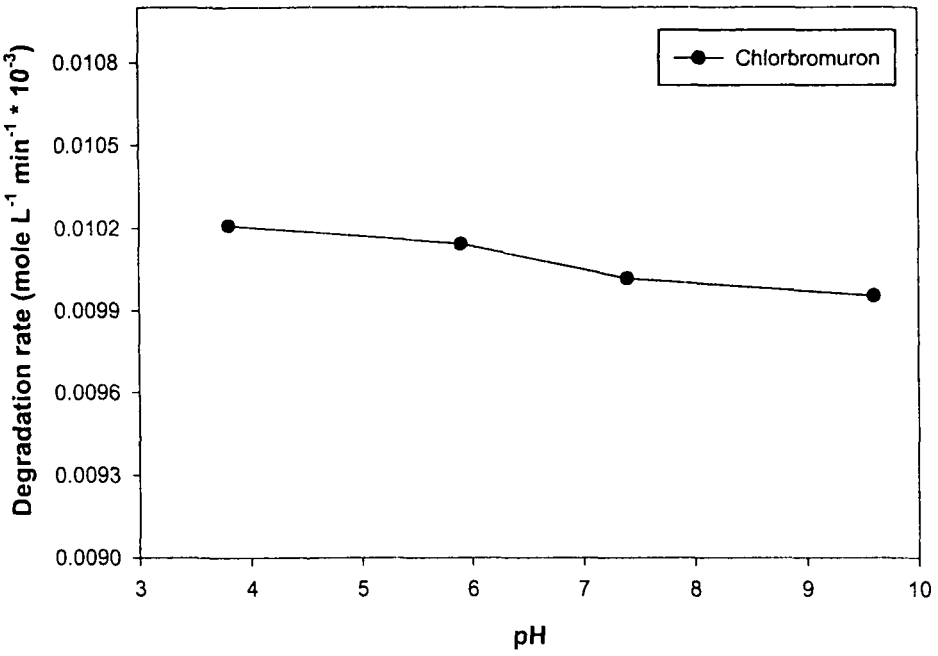


Figure 1.14. Influence of pH on the degradation rate for the decomposition of chlorbromuron (**3**).

Experimental conditions: 0.25 mM chlorbromuron, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (3.8, 5.9, 7.4 and 9.6), irradiation time = 60 min.

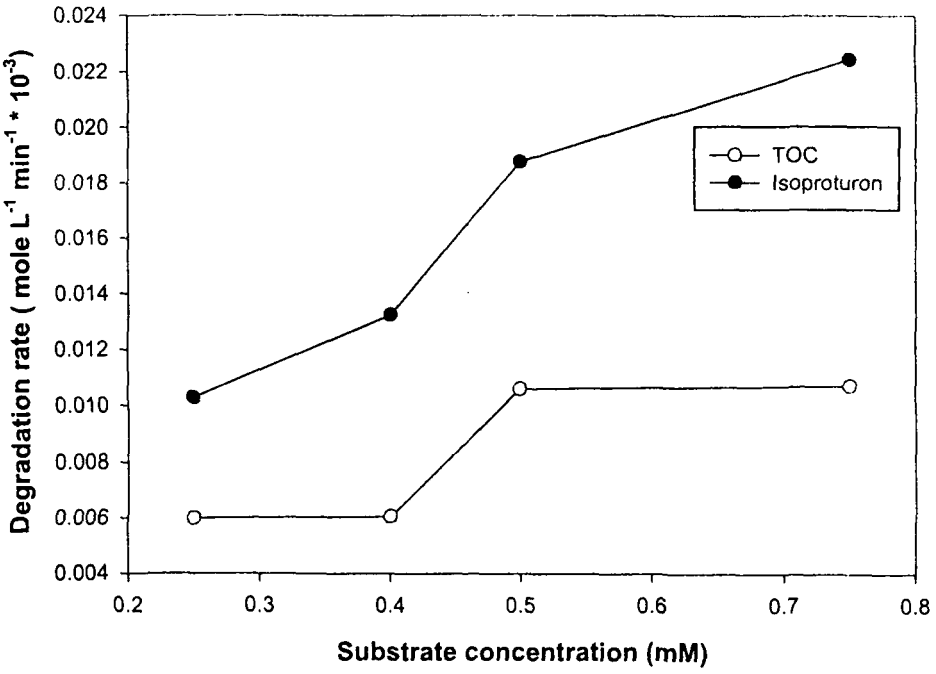


Figure 1.15. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of isoproturon (**1**).

Experimental conditions: substrate concentrations (0.25, 0.4, 0.5 and 0.75 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 80 min.

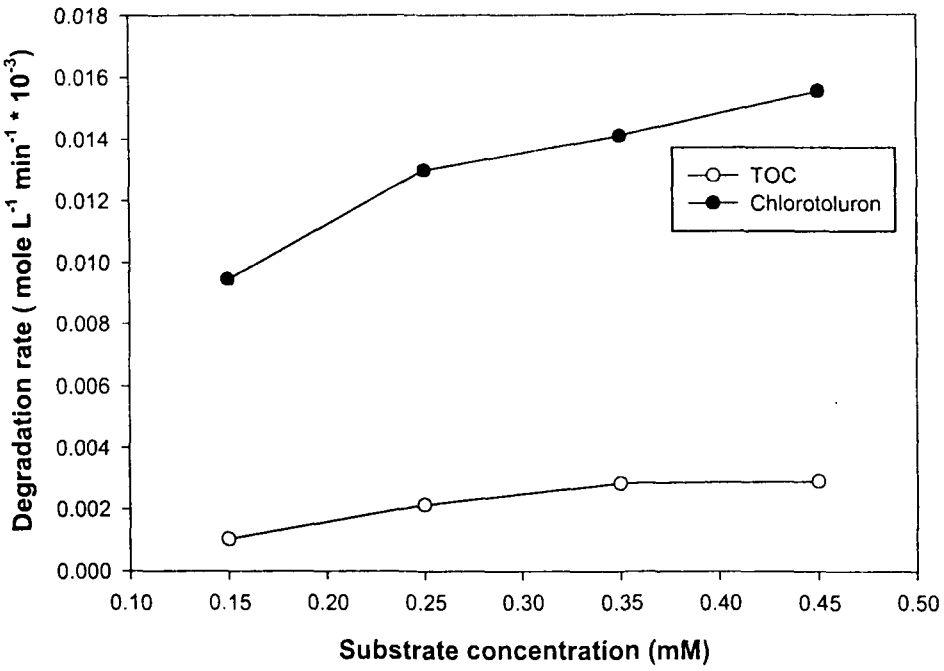


Figure 1.16. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of chlorotoluron (**2**).

Experimental conditions: substrate concentrations (0.15, 0.25, 0.35 and 0.45 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 120 min.

The rate for the decomposition of the pesticide derivative **3**, as a function of substrate concentration employing Degussa P25 is shown in Fig. **1.17**. The degradation rate markedly increases with the increase in substrate concentration from 0.15 to 0.35 mM, which levels off as the concentration increases from 0.35 to 0.5 mM.

As oxidation proceeds, less and less of the surface of the TiO_2 particle is covered as the pollutant is decomposed. Evidently, at total decomposition, the rate of degradation is zero and a decreased photocatalytic rate is to be expected with increasing irradiation time. It has been agreed, with minor variation that the expression for the rate of photomineralization of organic substrates with irradiated TiO_2 follows the Langmuir Hinshelwood (L-H) law for the four possible situations, i.e., a) the reaction takes place between two adsorbed substances, b) the reaction occurs between a radical in solution and an adsorbed substrate molecule, c) the reaction takes place between a radical linked to the surface and a substrate molecule in solution, and d) the reaction occurs with both the species being in solution. In all cases, the expression for the rate equation is similar to that derived from the L-H model, which has been useful in modeling the process, although it is not possible to find out whether the process takes place on the surface, in the solution or at the interface. Our

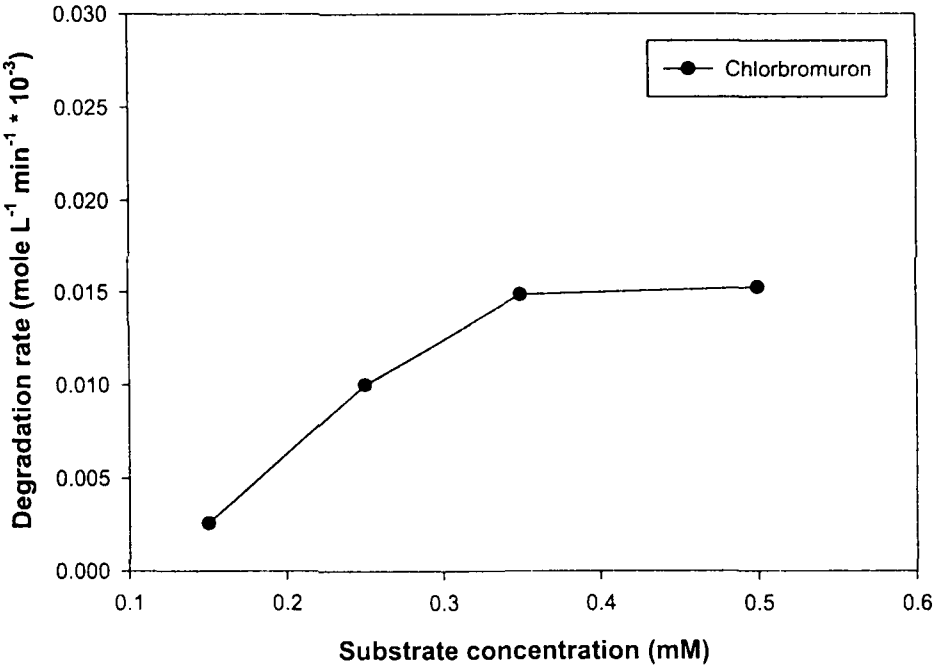


Figure 1.17. Influence of substrate concentration on the degradation rate for decomposition of chlorbromuron (3).

Experimental conditions: substrate concentrations (0.15, 0.25, 0.35, and 0.5 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 60 min.

results, on the effect of the initial concentration on the degradation rate are in agreement with the assumption of the Langmuir Hinshelwood model.

Earlier studies[40,41,44,49] on the photocatalytic degradation of colorless organic pollutants also indicate that the degradation rate increases with the increase in substrate concentration as observed in our results.

1.4.6 Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of pesticides under investigation was studied employing different concentrations of Degussa P25 varying from 0.5 to $3gL^{-1}$. The degradation rate for the TOC depletion and for the decomposition of the pesticide derivatives **1** and **2** as function of catalyst loading is shown in Figs. **1.18** and **1.19**, respectively. The degradation rate for the decomposition of the pesticide derivative **3** in the presence of different catalyst concentrations is shown in Fig. **1.20**.

As expected, the degradation rate was found to increase with the increase in catalyst concentration, which is the characteristic of heterogeneous photocatalysis. For pesticides derivative **1-3** the degradation rate gradually increases with the increase in catalyst concentration.

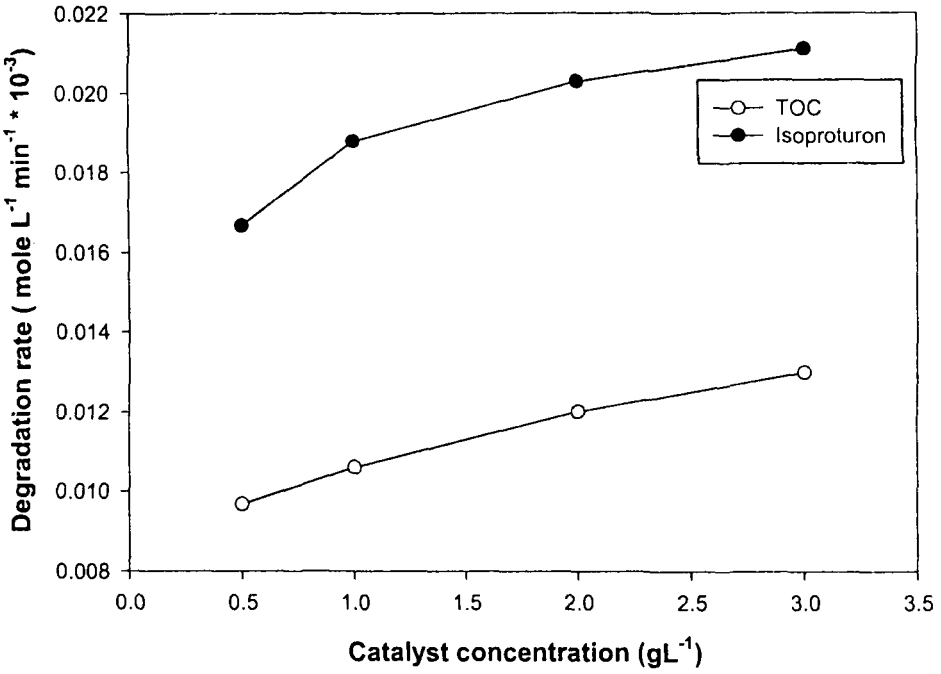


Figure 1.18. Influence of catalyst concentration on the degradation rate for the mineralization and for the decomposition of isoproturon (**1**).

Experimental conditions: 0.5 mM isoproturon, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 80 min.

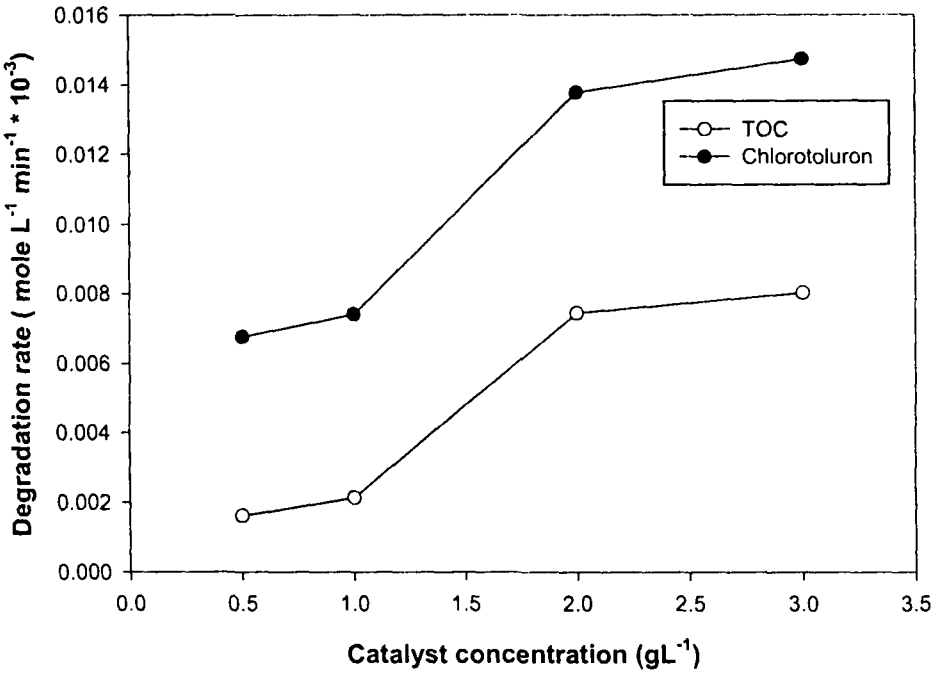


Figure 1.19. Influence of catalyst concentration on the degradation rate for the mineralization and for the decomposition of chlorotoluron (**2**).

Experimental conditions: 0.25 mM chlorotoluron, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 120 min.

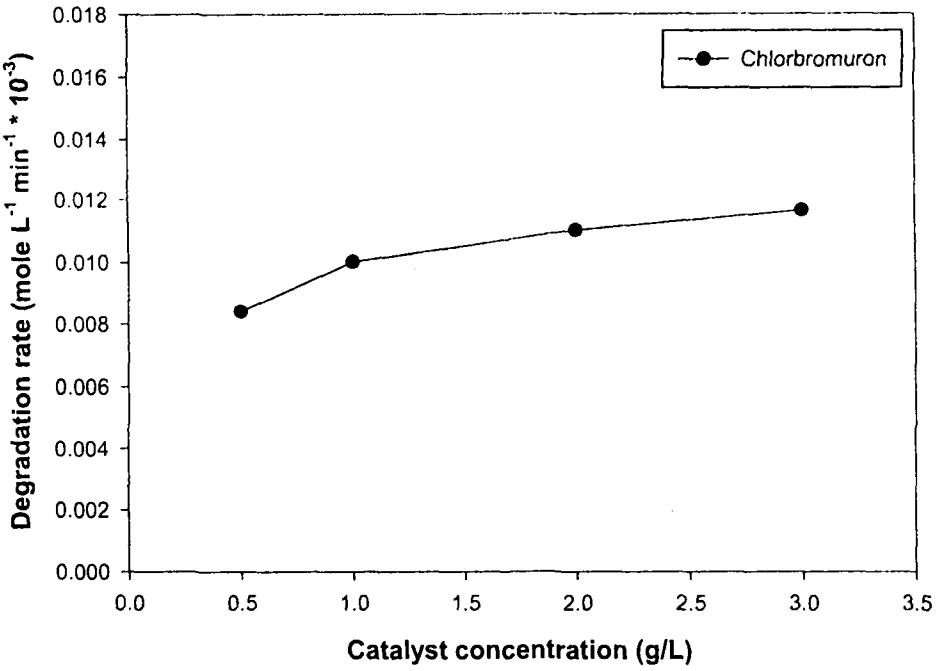


Figure 1.20. Influence of catalyst concentration on the degradation rate for decomposition of chlorbromuron (**3**). Experimental conditions: 0.5 mM chlorbromuron, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 60 min.

Whether in static, slurry, or dynamic flow reactors, the initial reaction rates were found to be directly proportional to catalyst concentration, indicating a heterogeneous regime. However, it was observed that above a certain concentration, the reaction rate decreases and becomes independent of the catalyst concentration. This limit depends on the geometry and working conditions of the photoreactor and for a definite amount of TiO_2 in which all the particles, i.e., surface exposed, are totally illuminated. When the catalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given application, this optimum catalyst concentration [$(TiO_2)_{OPT}$] has to be found, in order to avoid excess catalyst and insure total absorption of efficient photons. Our results on the effect of catalyst concentration on the degradation rate for the TOC depletion and decomposition of pesticides under investigation are in agreement with numerous studies reported in the literature.[40-42,44,49]

1.4.7. Effect of electron acceptors

One practical problem in using TiO_2 as a photocatalyst is the undesired electron / hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient and represent the major energy - wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron - hole pair recombination is to add other

(irreversible) electron acceptors to the reaction. They could have several different effects such as, i.e., 1) to increase the number of trapped electrons and, consequently, avoid recombination, 2) to generate more radicals and other oxidizing species, 3) to increase the oxidation rate of intermediate compounds and 4) to avoid problems caused by low oxygen concentration. In highly toxic wastewater where the degradation of organic pollutants is the major concern, the addition of electron acceptors to enhance the degradation rate may often be justified. With this view, the electron acceptor such as potassium persulphate, potassium bromate and hydrogen peroxide were added in the solution.

The degradation rate for the mineralization and decomposition of the pesticide derivatives **1** and **2** in the presence of different electron acceptors are shown in Figs. **1.21** and **1.22**, respectively. Fig **1.23** shows the rate for the decomposition of pesticide derivative **3** under analogous condition.

The electron acceptors such as hydrogen peroxide, bromate and persulphate ions are known to generate hydroxyl radicals by the mechanisms shown in eqs 6-10;

$$H_2O_2 + e^-_{CB} \rightarrow \dot{O}H + OH^- \quad [6]$$

$$BrO_3^- + 2H^+ + e^-_{CB} \rightarrow BrO_2^{\bullet} + H_2O \quad [7]$$

$$BrO_3^- + 6H^+ + 6\ e^-_{CB} \rightarrow [BrO_2^-, HOBr] \rightarrow Br^- + 3H_2O \quad [8]$$

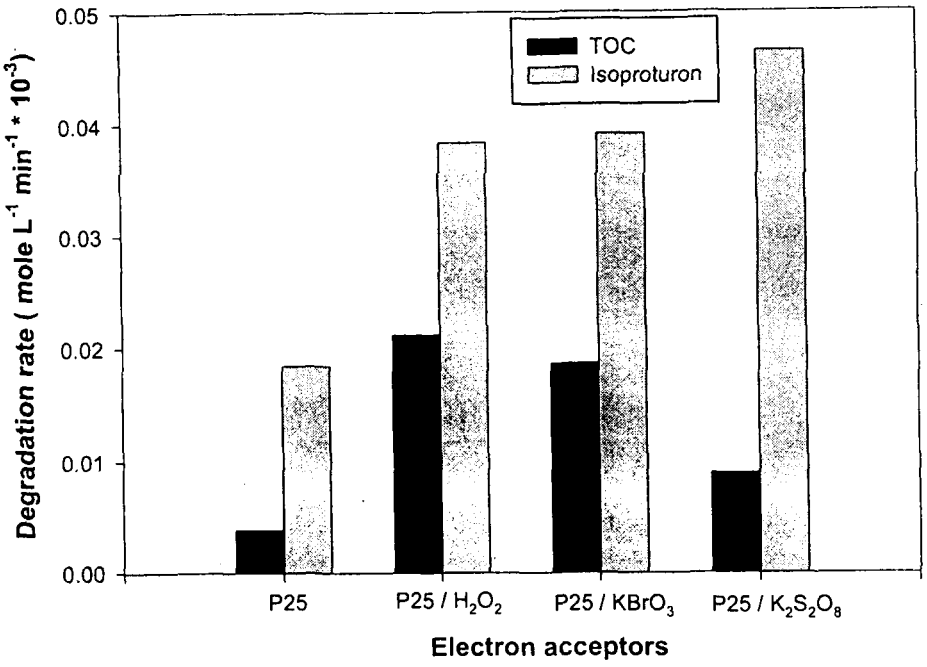


Figure 1.21. Comparison of degradation rate for the mineralization and for the decomposition of isoproturon (**1**) in the presence of different electron acceptors.
Experimental conditions: 1.5 mM isoproturon, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptors: $KBrO_3$ (5 mM), $K_2S_2O_8$ (5 mM), H_2O_2 (10 mM), irradiation time = 80 min.

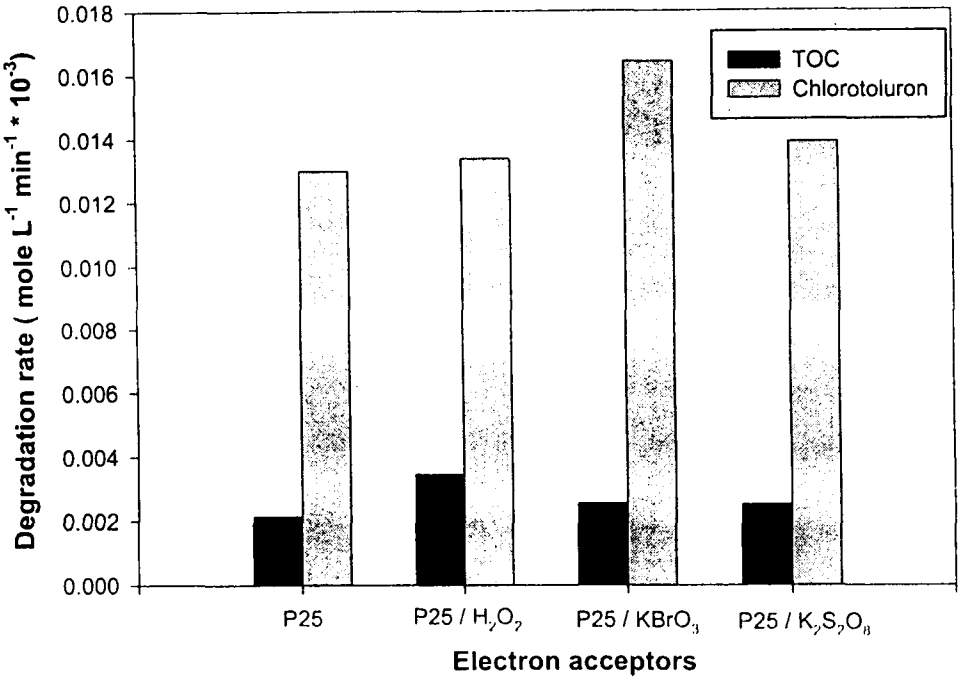


Figure 1.22. Comparison of degradation rate for the mineralization and for the decomposition of chlorotoluron (**2**) in the presence of different electron acceptors.
Experimental conditions: 0.25 mM chlorotoluron, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptors: $KBrO_3$ (5 mM), $K_2S_2O_8$ (5 mM), H_2O_2 (10 mM), irradiation time = 120 min.

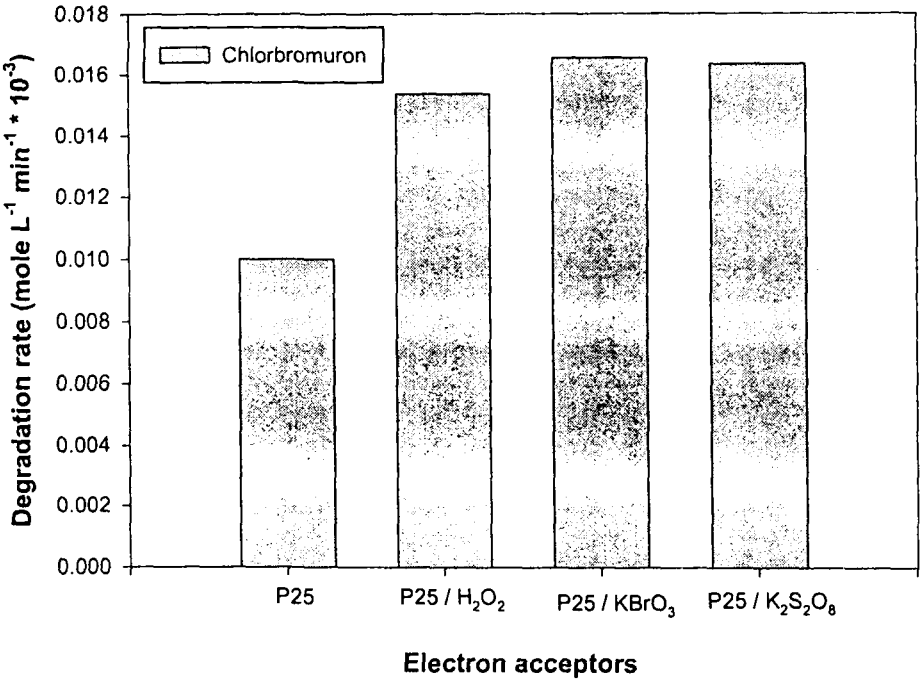


Figure 1.23. Comparison of degradation rate for the decomposition of chlorbromuron (**3**) in the presence of different electron acceptors.

Experimental conditions: 0.25 mM chlorbromuron, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptors: $KBrO_3$ (5 mM), $K_2S_2O_8$ (5 mM), H_2O_2 (10 mM), irradiation time = 60 min.

$$S_2O_8^{2-} + e^-_{cb} \rightarrow SO_4^{2-} + SO_4^{\bullet-} \quad [9]$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + \dot{O}H + H^+ \quad [10]$$

The respective one-electron reduction potentials of different species are: E ($O_2/O_2^{\bullet-}$) = -155mV, E ($H_2O_2/H\dot{O}$) = 800mV, E ($BrO_3^-/BrO_2^{\bullet}$) = 1150 mV, and E ($S_2O_8^{2-}/SO_4^{\bullet-}$) = 1100 mV.[50] From the thermodynamic point of view all employed additives should therefore be more efficient electron acceptors than molecular oxygen.

Among all the additives, potassium persulphate shows the better degradation rate for the decomposition while H_2O_2 shows better degradation rate for the mineralization of isoproturon (**1**) under analogous condition. In case of chlorotoluron (**2**), the additive potassium bromate showed a pronounced effect for the decomposition of the compound while H_2O_2 shows better mineralization rate as compared to other additives. For chlorbromuron (**3**), the all additives showed the beneficial effect.

The effective electron acceptor ability of $KBrO_3$ has been observed in number of studies before.[41,42,51] The reason can be attributed to the number of electrons it reacts as shown in eq. 8. Another possible explanation might be a change in the reaction mechanism of the photocatalytic degradation. Since the reduction of bromate ions by electrons does not lead directly to the formation of hydroxyl radicals, but

rather to the formation of other reactive radicals or oxidizing agents eg. BrO_2 and HOBr. Furthermore, bromate ions by themselves can act as oxidizing agents. Linder has proposed a mechanism for the photocatalytic degradation of 4-chlorophenol in the presence of bromate ions considering direct oxidation of the substrate by bromate ions.[52] A similar mechanism might also be operative in the model compounds **2** and **3** under investigation.

The enhanced effect of persulphate ion on the degradation of pollutants may be accounted on the basis that persulphate is a beneficial oxidizing agent in photocatalytic detoxification because SO_4^- is formed from the oxidant by reaction with the electron generated at conduction band (e^-_{cb}) of the semiconductor as shown in eq. 9. This sulphate radical anion (SO_4^-) is a strong oxidant (E^0 = 2.6 eV) and it can react with the organic pollutants in three possible modes 1) by abstracting a hydrogen atom from saturated carbon. 2) by adding to unsaturated or aromatic carbon and 3) by removing one electron from the carboxylate anions and from certain neutral molecules. In spite of this sulphate radical anion can trap the photogenerated electrons and/ or generated hydroxyl radical as shown in eq. 10. The formation of sulphate radical anion and hydroxyl radical are powerful oxidant, which can degrade the organic pollutants at a faster rate.

The effect of H_2O_2 has been investigated in numerous studies and it was observed that it increases the photodegradation rates of organic pollutants.[53-55] The enhancement of the degradation rate on addition of H_2O_2 can be rationalized in terms of several reason. Firstly, it increase the rate by removing the surface-trapped electrons, there by lowering the electron-hole recombination rate and increasing the efficiency of hole utilization for reactions such as ($OH^- + h^+ \longrightarrow OH$). Secondly, H_2O_2 may split photolytically to produce OH radicals directly, as cited in studies of homogeneous photooxidation using UV / (H_2O_2 + O_2).[56] Thirdly, the solution phase may at times be oxygen starved, because of either oxygen consumption or slow oxygen mass transfer, and peroxide addition thereby increase the rate towards what it would have been had an adequate oxygen supply been provided.

During the photocatalytic degradation the free radical formed serve a dual function. They are not only the strong oxidants but also at the same time their formation and subsequent rapid oxidation reactions inhibit the electron hole pair recombination.

1.4.8 Photolysis of TiO_2 suspension containing isoproturon under sunlight

For practical applications of wastewater treatment based on these processes, the utilization of sunlight is preferred. Hence the aqueous

suspension of TiO_2 containing isoproturon was exposed to solar radiation. Fig. **1.24** shows the change in absorption intensity at 238 nm as a function of irradiation time on illumination of an aqueous suspension of isoproturon (0.5 mM) in the presence of TiO_2 (P25, $1gL^{-1}$) under sunlight and UV light source. It was found that the degradation of the model compound proceeds much more rapidly in the presence of UV light source as compared to sunlight source.

1.4.8 Intermediate products

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the pesticide derivatives **1** and **2** in aqueous suspension of titanium dioxide through GC/MS analysis.

An aqueous suspension of isoproturon (**1**, 0.3 mM, 250 mL) was irradiated with a 450 W high-pressure mercury lamp in the presence of TiO_2 (Degussa P25, 1.5 gL^{-1}) under constant bubbling of air for 2 h. The catalyst was removed through centrifugation and irradiated aqueous solution was extracted with methylene chloride, which was dried over anhydrous sodium sulphate. The GC/MS analysis of the organic extract showed the formation of 4-isopropyl-phenylurea (**10**), 4-isopropylaniline (**11**) and 1,1-dimethyl-3-phenylurea (**9**) appearing at retention times (t_R)

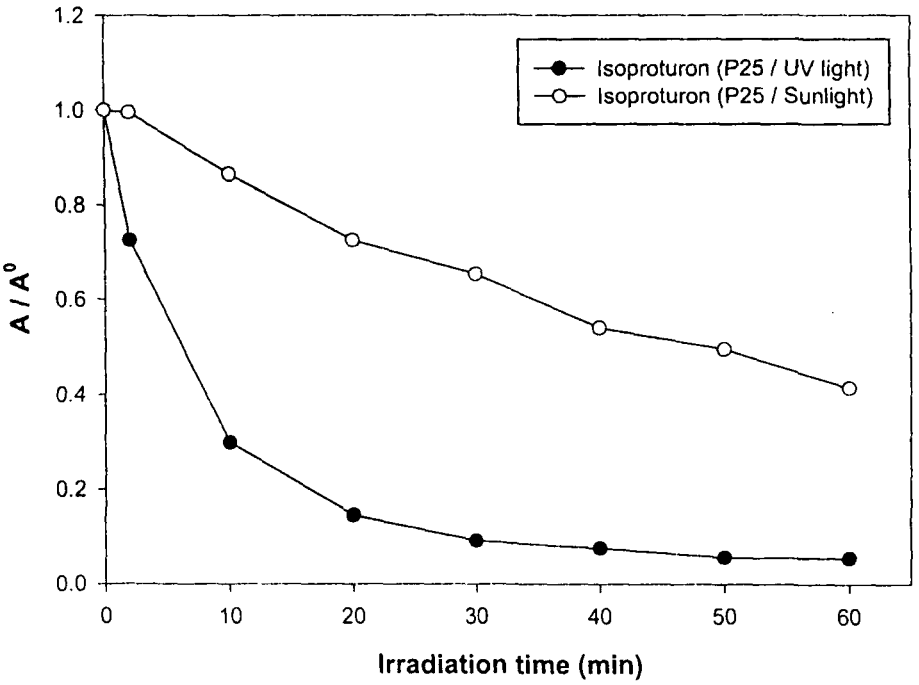


Figure 1.24. Change in absorption intensity as a function of irradiation time for an aqueous suspension of isoproturon (**1**) in the presence of photocatalyst under sunlight and UV light source.

Experimental conditions: a) UV Light: 0.5 mM isoproturon, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 1 h.

b) Sunlight: 0.5 mM isoproturon, V=250 mL, round bottom flask (250 mL), photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}) cont. O_2 purging and stirring, irradiation time = 1 h.

9.805 min, 10.478 min and 11.452 min, respectively, along with some unchanged starting material appearing at (t_R) 5.035 min.

It is pertinent to mention here that the model compound did not show the molecular ion peak, instead it showed the peak equivalent to the loss of $N(CH_3)_2$ group. The products were characterized by comparing the molecular ion and mass fragmentation pattern with those reported in the GC/MS library, as indicated below:

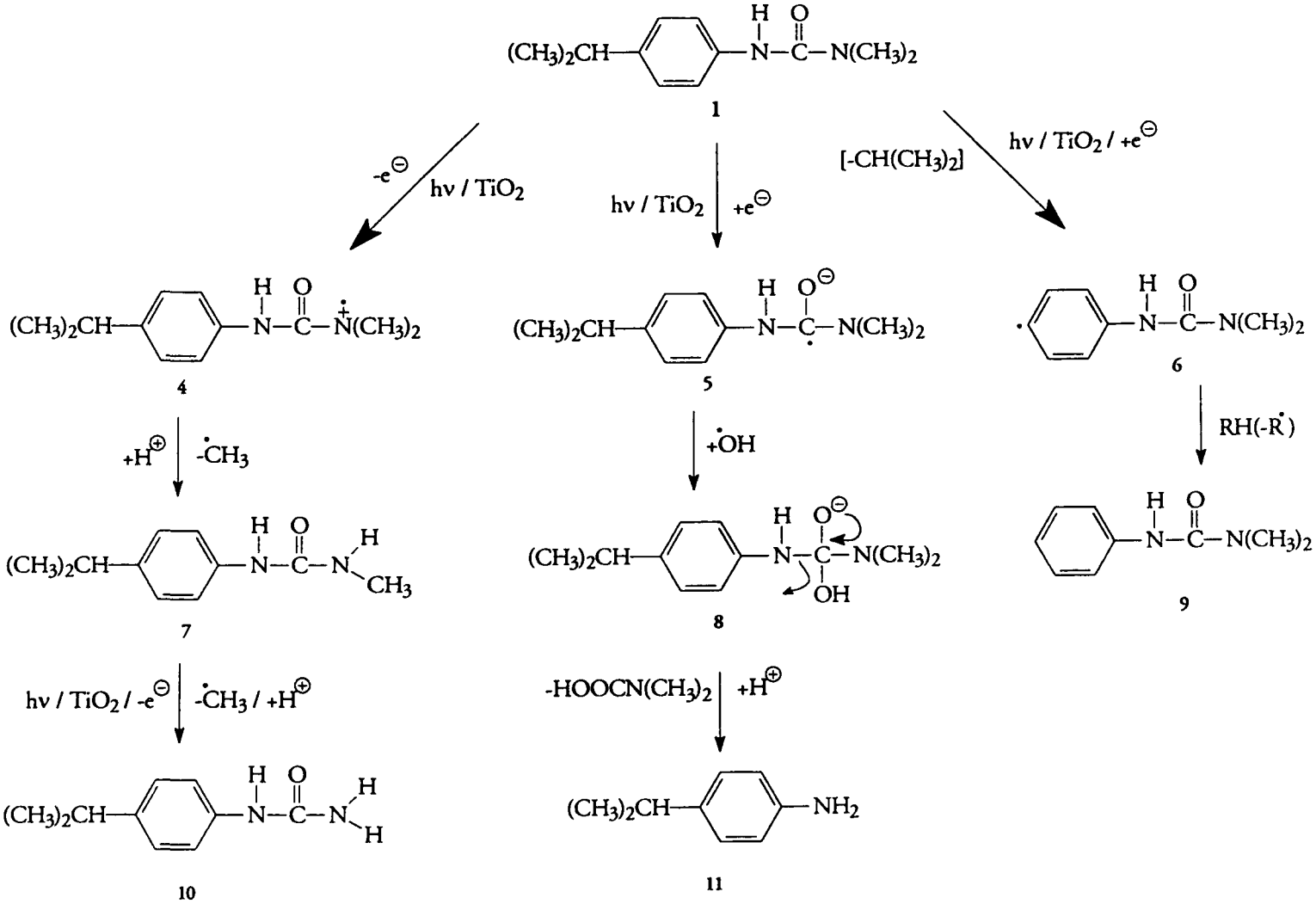
Compound 10 : 178 (M^+), 161, 146, 128, 118, 104, 84, 72, 63, 44 and 41

Compound 11 : 135 (M^+), 120, 103, 91, 77, 58, 49 and 41

Compound 9 : 164 (M^+), 148, 135, 119, 106, 91, 72, 65, 44 and 39

Compound 1 : 161 (M^+, -$N(CH_3)_2$), 146, 128, 118, 103, 91, 77, 58, 51 and 41

The formation of products **10**, **11** and **9** from **1** could be understood in terms of the pathways shown in Scheme **1.1**. The model compound **1**, upon the transfer of an electron can formed the radical cationic species **4** or can abstract an electron to give the radical anionic species **5**. Alternatively, the compound **1**, can also undergo loss of isopropyl group to give a radical species **6**. The radical cationic species **4**, undergo the loss of methyl radical, subsequently by abstraction of proton may give rise to the product 1-(4-isopropyl-phenyl)-3-methylurea (**7**), which may undergo



Scheme 1.1

similar reaction to loose another methyl group to give the observed product **10**. The radical anionic species **5** may undergo addition of a hydroxyl radical followed by the loss of $N(CH_3)_2COOH$ group followed by abstraction of a proton to give the observed product **11**. The radical species **6** on abstraction of hydrogen atom from solvent may give rise to the product **9**.

The irradiation of an aqueous suspension of chlorotoluron (**2**, 0.35 mM, 250 ml) in the presence of TiO_2 (Degussa P25, 1.5 gL^{-1}) under constant bubbling of air for 2 h and work up of the reaction mixture under analogous conditions followed by GC/MS analysis of the irradiated mixture showed the formation of (3-chloro-4-methyl-phenyl) urea (**18**) and 3-chloro-4-methyl-phenylamine (**19**) appearing at retention times (t_R)10.255 min and 5.520 min, respectively along with some unchanged starting material (**2**) appearing at (t_R) 5.097 min. It is pertinent to mention here that the model compound did not show the molecular ion peak, instead it showed the peak equivalent to the loss of $N(CH_3)_2$ group. The products were characterized by comparing the molecular ion and mass fragmentation pattern with those reported in the GC/MS library, as indicated below:

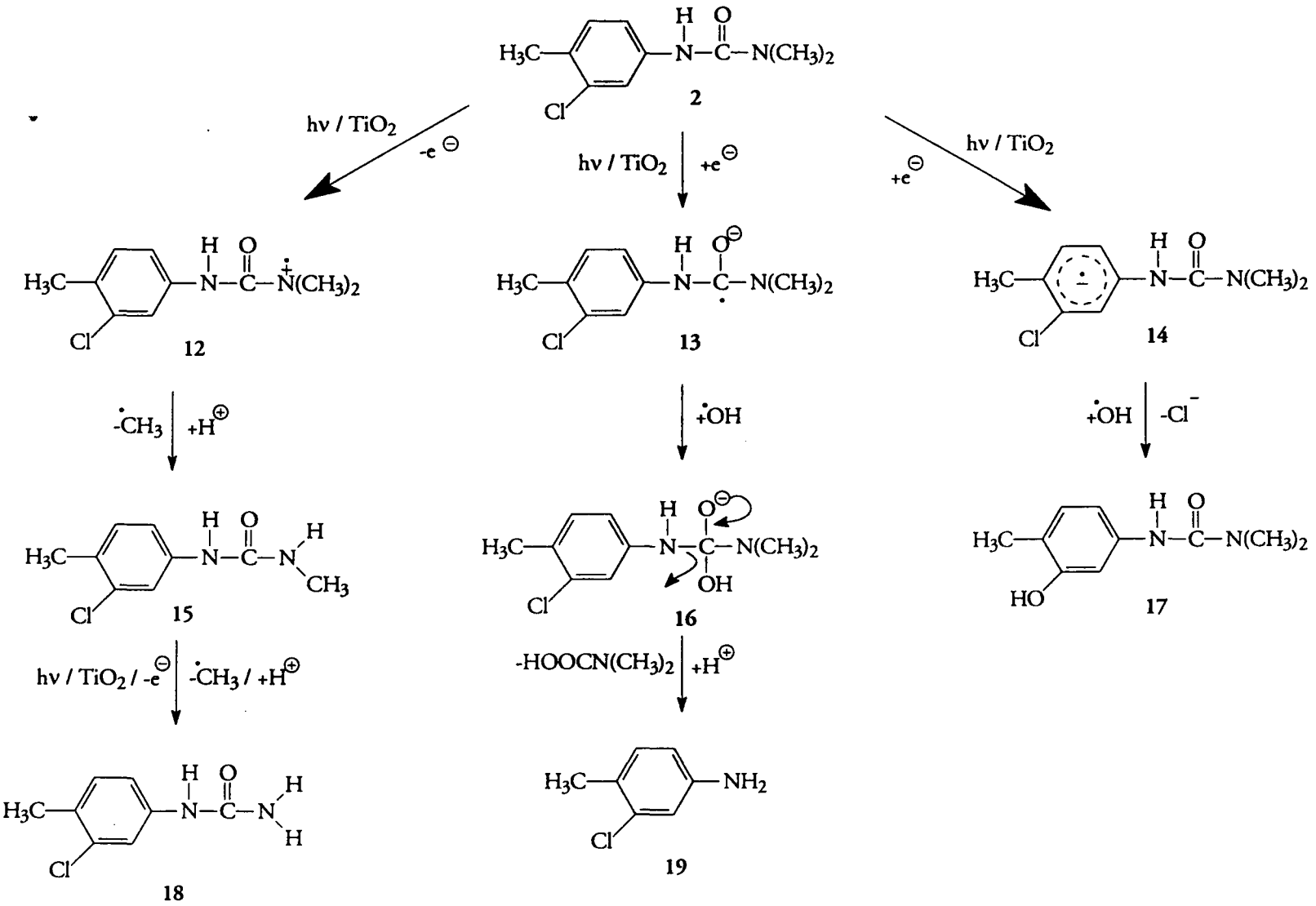
Compound 18 : 184 (M^+), 155, 148, 127, 112, 102, 92, 77, 65, 45 and 40

Compound 19 : 141 (M^+), 132, 113, 106, 84, 77, 63, 49 and 41

Compound 2 : 169 (M^+, $-N(CH_3)_2$), 167, 140, 132, 125, 104, 85, 77, 63, 51 and 40

When the reaction of this model compound was carried out in the presence of Hombikat UV 100, a difference in the yield of the above two products was observed with that of the Degussa P25.

A possible mechanism for the formation of products **17**, **18**, and **19** from chlorotoluron (**2**) involving electron transfer reaction and reaction with hydroxyl radicals could similarly be understood in terms of pathways shown in Scheme **1.2**.


hν / TiO2
-e⊖
hν / TiO2
+e⊖
hν / TiO2
+e⊖
2
12
13
14
-CH3
+H⊕
+OH
+OH
-Cl⁻
15
16
17
hν / TiO2 / -e⊖
-CH3 / +H⊕
-HOOCN(CH3)2
+H⊕
18
19

Scheme 1.2

References:

1 M. M. Haque and M. Muneer, *J. Environ. Manag.*, 69 (**2003**) 169.

2 M. M. Haque and M. Muneer, *Environ. Toxicol. Chem.* (communicated).

3 M. M. Haque and M. Muneer, *Asian J. Environ. Poll.* (communicated)

4 World Resources Institute 1994-95, N.Y.O., **1994**.

5 O. Ligrini, E. Oliveros and A. Braun, *Chem. Rev.,* 93 (**1993**) 671.

6 S. Parra, Coupling of photocatalytic and biological processes as a contribution to the detoxification of water: catalytic and technological aspects Ph.D. Thesis, Chimiste, Universidad del Valle, Cali, Colombie, 2001.

7 R. M. Dowd, M. P. Anderson and M. L. Johnson, Proceedings of the Second National Outdoor Action Conference on Aquifer Restoration, Groundwater Monitoring Geophysical Methods, National Water Well Association, Dublin, OH, **1998**, p. 1365.

8 D. M. Blake, Bibliography of work on the photocatalytic Removal of Hazardous Compounds from Water and Air, National Renewal Energy Laboratory, USA, **2001**.

9 X. Zhao, X. Quan, H. Zhao, Shuo Chen, Y. Zhao and J. Chen, *J. Photochem. Photobiol. A: Chem.,* 167 (**2004**) 177.

10 M. Karkmaz, E. Puzenat, C. Guillard and J. M. Herrmann, *Appl. Catal. B: Environ.*, 51 (**2004**) 183.

11 R. R. Ishiki, H. M. Ishiki and K. Takashima, *Chemosphere*, 58 (**2005**) 1461.

12 C. Lung-Chuan, T. Fu-Ren and H. Chao-Ming, *J. Photochem. Photobiol. A: Chem.*, 170 (**2005**) 7.

13 P. Robertson, J. Cleaner Prod., 4 (**1996**) p. 203.

14 M. A. Fox and M. T. Dulay, *Chem. Rev.*, 93 (**1993**) 341.

15 M. A. Fox and Nouveau, *J. de Chimie.*, 11 (**1987**) 129.

16 D. Bahnemann, D. Bockelmann and R. Goslich, *Sol. Ener. mat.*, 24 (**1991**) 564.

17 C. Tomlim, The Pesticide Manual, 10 ed., The Bath Press, **1994**, p. 611.

18 K. A. Hassal, The Biochemistry and uses of pesticides, Macmillan Press Ltd, Hampshire, **1990**.

19 C. Tixier, L. Meunier, F. Bonnemoy, and P. Boule, *Int. J. Photoenergy*, 2 (**2000**)1.

20 P. Dureja, S. Walia, and K. K. Sharma, *Toxicol. Environ. Chem.*, 34 (**1991**) 65.

21 C. De St-Laumer, C. Emmelin, and P. Meallier, *Fresenius Environ. Bull.*, 6 (**1997**) 529.

22 S. Parra, S. Malato, and C. Pulgarin, *Appl. Catal. B: Environ.*, 36 (**2002**) 131.

23 Y. A. Madhun and V. H. Freed, *Chemosphere*, 16 (**1987**) 1003.

24 The pesticide chlorotoluron was a gift sample from P. Boule, Laboratoire de Photochimie Moléculaire et Macromoleculaire (UMR 6505), Université Blaise Pascal (Clermont-Ferrand), F-63177 Aubiére, cedex France.

25 The photocatalyst Degussa P25 was a gift sample from Degussa-Huls, Frankfurt/Main, Germany.

26 The photocatalyst Hombikat UV100 and PC500 was a gift sample from Dr. D. Bahnemann from the Institut fuer Technische Chemie Universitat Hannover Callinstrasse, Hannover, Germany.

27 The photocatalyst TTP was obtained from Travancore Titanium Products, Kerala, India.

28 R. I. Bickley, T. G. Carreno, J. S. Lees, L. Palmisano and R. J. D. Tilley, *J. Solid State Chem.*, 92 (**1992**) 178.

29 M. Lindner, D. Bahnemann, B. Hirthe and W. D. Griebler, *J. Sol. Energy Eng.*, 119 (**1997**) 120.

30 S. Rauer, Untersunchung von kommerziell erhaltlichen Titandioxiden hinsichtlich ihrer photokatalytischen Aktivtat, Diplomarbeit, fachhochschule Hannover, Fachbereich Maschinenbau Vertiefung Umwelt-und Verfahrenstechnil, Hannover, Germany, **1998**.

31 TheTotal Organic Carbon Analyzer was a gift equipment from Alexander von Humboldt-Stiftung, Bonn, Germany.

32 GC/MS analysis was done by Dr. M. Muneer at The Institut fuer Technische Chemie, Universitat Hannover, Germany.

33 J. C. D'Oliveira, *J Photochem Photobiol A: Chem.*, 72 (**1993**) 261.

34 K. E. O'Shea and C. Cardona, *J. Org. Chem.*, 59 (**1994**) 5005.

35 L. Amalric, *Water Res.*, 30 (**1996**) 1137.

36 B. Sangchakr, T. Hisanaga, and K. Tanaka, *J. Photochem. Photobiol. A: Chem.*, 85 (**1995**) 187.

37 J. M. Tseng and C. P. Huang, *Water Sci. Technol.*, 23 (**1991**) 377.

38 D. Weichgrebe and A. Vogelpohl, Stratgie zur Auswahl geeigneter Oxidationsverfahren. 2. Fachtagung Naboxidative Abwasserbehadlung, Clausthal, **1995**.

39 S. T. Martin, H. Hermann, W. Choi and M. R. Hoffmann, *J. Chem. Soc. Faraday Trans.*, 90 (**1994**) 3315.

40 M. Muneer, J. Theurich and D. Bahnemann, *J. Photochem. Photobiol. A: Chem.*, 143 (**2001**) 213.

41 M. Muneer and D. Bahnemann, *Water Sci. Technol.*, 144 (**2001**) 331.

42 M. Muneer, J. Theurich and D. Bahnemann, *Res. Chem. Intermed.*, 25 (**1999**) 667.

43 M. Lindner, D. Bahnemann, B. Hirthe, W. D. Griebler, Novel TiO_2 powders as highly active photocatalysts. In Solar Water Detoxification; Solar Engineering, Stine, W. B.; Tanaka, T.; Claridge, D.E., Eds.; ASME: New York, **1995**, 339.

44 M. Muneer, H. K. Singh and D. Bahnemann, *Chemosphere*, 49 (**2002**) 193.

45 M. Saquib and M. Muneer, *Dyes and Pigm.*, 53 (**2002**) 237.

46 D. C. Hurum, A. G. Agrios, K. A. Gray, T. Rajh and M. C. Thurnauer, *J. Phy. Chem. B*, 107 (**2003**) 4545.

47 A. J. Nozik, in : D. F. Ollis, H. EL-Ekabi (Eds.), Photocatalytic Purification and Treatment of water and Air, Elsevier, Amsterdam, **1993**, p. 391.

48 H. Weller, *Angew. Chem. Int. Ed. Eng.*, 32 (**1993**) 41.

49 H. K. Singh, M. Muneer and D. Bahnemann, *Photchem. Photobiol. Sci.*, 2 (**2003**) 151.

50 P. Wardman, *J. Phys. Chem.*, Ref. Data, 18 (**1989**) 1637.

51 S. Nevim, H. Arzu, K. Gulin and Z. Cinar, *J. Photochem. Photobiol. A: Chem.*, 139 (**2001**) 225.

52 M. Linder, Ph.D. Thesis, Department of Chemistry, University of Hannover, Hannover, Germany, **1997**.

53 Y. T. Wei and C. Wan, *J. Photochem. Photobiol. A: Chem.,* 55 (**1992**) 241.

54 Y. T. Wei, Y. Y. Wang and C. Wan, *J. Photochem. Photobiol. A: Chem.,* 55 (**1992**) 241.

55 M. Hallamn, *J. Photochem. Photobiol. A: Chem.,* 66 (**1992**) 215.

56 G. R. Peyton and W. H. Glaze, *Environ. Sci. Technol.,* 22 (**1988**) 761.

Chapter 2

PHOTOCATALYSED DEGRADATION OF FOUR SELECTED CARBAMATE DERIVATIVE PESTICIDES, THIRAM, CARBARYL, ZINEB AND SODIUM DIETHYLDITHIOCARBAMATE IN AQUEOUS SUSPENSION OF SEMICONDUCTOR[1,2]

2.1 Abstract

The photocatalysed degradation of four selected carbamates derivative pesticides, such as thiram (**1**), carbaryl (**2**), zineb (**3**) and sodium diethyldithiocarbamate (**4**) have been investigated in aqueous suspensions of titanium dioxide under a variety of conditions. The degradation was investigated by monitoring the change in substrate concentration employing UV-spectroscopic analysis technique and depletion in Total Organic Carbon (TOC) content as a function of irradiation time. The degradation of the pesticides were studied under different conditions such as different types of TiO_2, pH, catalyst concentration, substrate concentration and in the presence of electron acceptors such as hydrogen peroxide, ammonium persulphate and potassium bromate besides molecular oxygen. The degradation rates were found to be strongly

influenced by all the above parameters. The degradation of thiram (**1**) was also investigated under sunlight and the efficiency of the degradation was compared with that of the artificial light source. The photocatalyst Degussa P25 was found to be more efficient for the degradation of all four pesticides under investigation. An attempt was made to identify the degradation products formed during the photooxidation processes through GC/MS analysis technique and probable mechanism for the formation of products has been proposed.

2.2 Introduction

Another class of pesticide, which is used extensively in the agriculture field, is the carbamates, which constitutes an important class of insecticides. They are widely used against pest on vast forest areas because they have a rapid action and usually exhibit a moderate persistence in the environment.

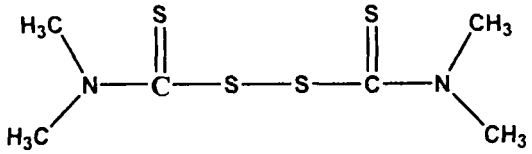
The model compound thiram (**1**) is a toxic compound, belongs to ethylene bisdithiocarbamate (EBDC) chemical class. The EBDCs are fungicides used to prevent crop damage in the field and to protect harvested crops from deterioration in the storage or transport.[3] Thiram is used as a seed protectant and to protect fruit, vegetable and ornamental

from a variety of fungal diseases. It is also used as an animal repellent to protect fruit trees and ornamentals from damage by rabbits, rodents and deer. The soil half-life for thiram is reported as 15 days.[4]

Carbaryl (1-naphthyl N-methylcarbamate) is an important member of carbamate. It shows a relatively short residual life time (few weeks in soils), its biological half life is usually larger (e.g. 5-6 months in fishes)[5], and some of its toxic metabolites are rather persistence in the environment (until 1-4 months).[6] The continuous flow degradation of carbaryl under UV light irradiation[7] and solar light[8] using TiO_2 has been reported earlier.

The direct photolysis[9,10] and photocatalysed degradation[11] of thiram has also been studied earlier. Inspite of these studies, no major effort has been made to study the detail degradation kinetics of the model pollutant under photocatalytic conditions. Therefore, we have undertaken a detailed investigation on the photocatalysed degradation of four selected carbamates derivative pesticides such as thiram (**1**), carbaryl (**2**), zineb (**3**) and sodium diethyldithiocarbamate (**4**) (Chart **2.1**) in aqueous suspension of TiO_2 under a variety of conditions e.g. pH, substrate and catalyst concentrations, types of photocatalyst and addition of electron acceptors. An attempt has also been made to identify the degradation products

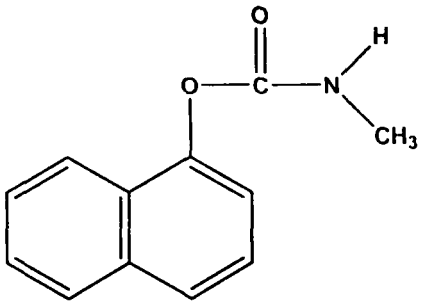
formed during the photooxidation process through GC/MS analysis technique.



Thiram

$C_6H_{12}S_4N_2$

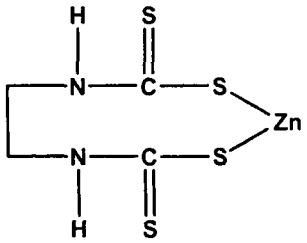
1



Carbaryl

$C_{12}H_{11}NO_2$

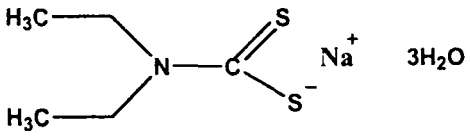
2



Zineb

$C_4H_6S_4N_2Zn$

3



Sodium diethyldithiocarbamate trihydrate

$C_5H_{10}S_2NNa\ 3H_2O$

4

Chart 2.1 Chemical structure, name, and chemical formula.

2.3 Experimental

2.3.1 Reagent and chemicals

Thiram (**1**) was obtained from Swarop Chemicals Pvt. Ltd Lucknow, India whereas carbaryl (**2**) and zineb (**3**) was purchased from Indofil Chemical Company, Mumbai, India. The pesticide derivative, sodium diethyldithiocarbamte (**4**) was purchased from Qualigens Fine Chemicals, Bombay, India. All the compounds were used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst titanium dioxide, Degussa P25 (Degussa AG)[12] was used in most of the experiments, whereas other catalyst powders namely Hombikat UV100 (Sachtleben chemie GmbH)[13], PC500 (Milenium inorganic chemicals)[13] and TTP (Travancore titanium products, India)[14] were used for comparative studies. The other chemicals used in this study such as sodium hydroxide, nitric acid, ammonium persulphate, hydrogen peroxide and potassium bromate were obtained from Merck.

1.3.2 Procedure

For experiments under UV light, the desired concentrations of compounds **1-4** were prepared in double distilled water and an immersion well photochemical reactor made of Pyrex glass was used. For irradiation

experiments 250 mL solution of desired concentration was filled into the reactor and required amount of TiO_2 was added. The solution was stirred for at least 15 minutes in the dark to allow equilibration of the system, so that the loss of compound due to adsorption can be taken into account. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp. IR and short wavelength UV radiations were eliminated by a water circulating Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during the irradiation for analysis after centrifugation.

The sunlight experiments were carried out between 9:00 A.M to 2:30 P.M during the month of June at Aligarh City which is about 140 Km from New Delhi. Reactions were carried out in a round bottom flask (250 mL) made of Pyrex glass. The solution (250 mL) of desired concentration of the model compound containing required amount of photocatalyst was taken and stirred for 15 min in the dark in presence of oxygen for equilibration. The solution was then placed on flat platform with continuous stirring and

purging of molecular oxygen under sunlight. Samples (10 mL) were collected before and at regular intervals during the illumination for analysis.

2.3.2 Analysis

The degradation of the pesticide derivatives, **1-4** was followed by measuring the decrease in absorption intensity at their λ_{max} as a function of irradiation time using Shimadzu UV-Vis Spectrophotometer (Model 1601). The mineralization of the pesticide derivative **2-4** was monitored by measuring the depletion in TOC content as function of irradiation time using Shimadzu 5000 A TOC Analyzer.[15]

1.3.3.3 Characterization of intermediate products[16]

For the characterization of intermediate products, aqueous solutions (250 mL) of all the pesticide containing TiO_2 (Degussa P25, 1 gL^{-1}) was taken in an immersion well photochemical reactor made of Pyrex glass. The mixture was irradiated with a 125 W medium pressure mercury lamp for a required period of time. The photocatalyst was removed through filtration and the filtrate was extracted with chloroform, which was subsequently dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure to give a residual mass, which was analyzed by GC/MS analysis technique. For GC/MS analysis a Hewlett

Packard Gas Chromatograph and Mass Spectrometer (G1800 A) equipped with a 30 m HP-1 (d = 0.25 mm) capillary column, operating temperature programmed (injection temperature 100 ^{0}C which is raised to 250 ^{0}C at the rate of 10 ^{0}C min^{-1} which is further raised to 280 ^{0}C at the rate of 30 ^{0}C *min^{-1}) in splitless mode injection volume* 0.5 μL *with helium as a carrier gas* was used.

2.4 Results and Discussion

2.4.1 Irradiation of an aqueous suspension of pesticides containing TiO_2

Irradiation of an aqueous suspension of desired concentration of the pesticides under investigation in the presence of TiO_2 (Degussa P25, 1gL^{-1}) with a 125 W medium pressure mercury lamp under oxygen atmosphere lead to decrease in absorption intensity and depletion in TOC content as a function of irradiation time. Fig. **2.1** shows the change in absorption intensity as a function of time for irradiation of an aqueous suspension of thiram (**1**) in the presence and absence of photocatalyst. Figs. **2.2 - 2.4** show the change in absorption intensity and depletion in TOC contents as a function of time in the presence and absence of the photocatalyst for the irradiation of pesticide derivatives **2-4**, respectively. It

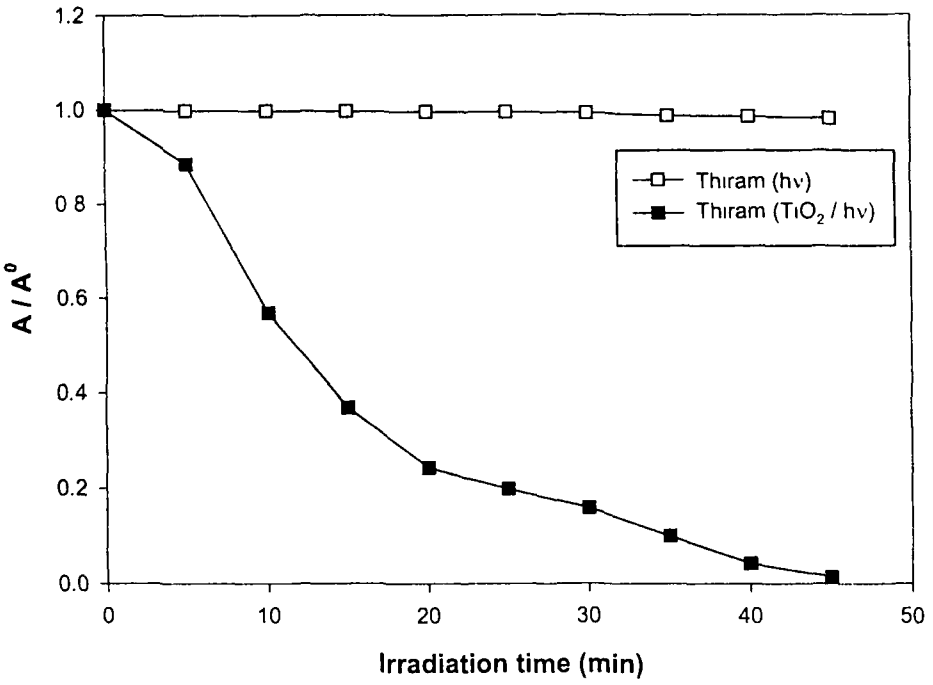


Figure 2.1. Change in absorption intensity at 278 nm as a function of irradiation time for an aqueous solution of thiram (**1**) in the presence and absence of photocatalyst.

Experimental conditions: 0.5 mM thiram, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 45 min.

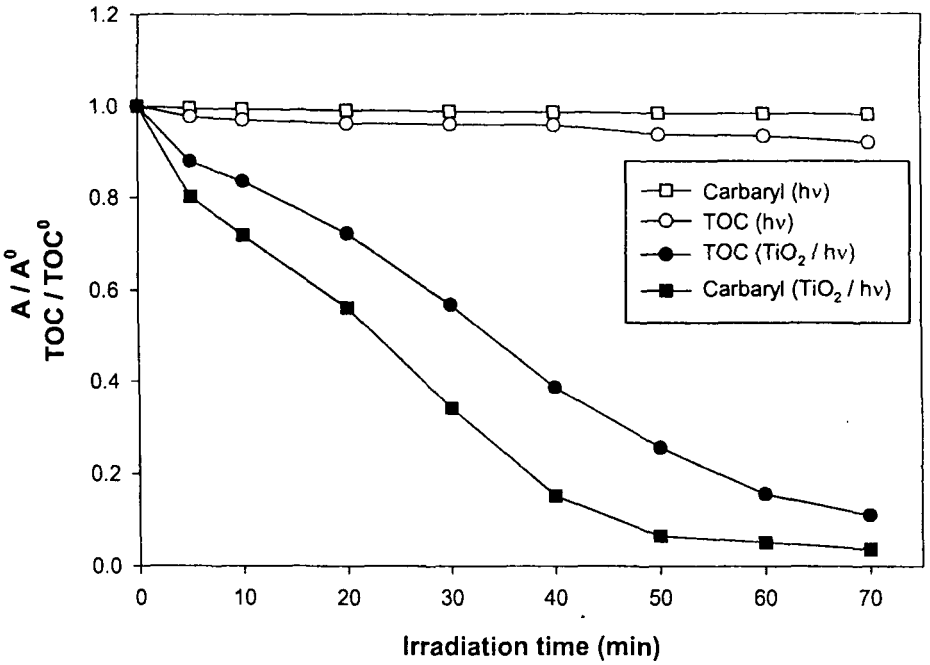


Figure 2.2. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of carbaryl (**2**) in the presence and absence of photocatalyst.

Experimental conditions: 0.5 mM carbaryl, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 238 nm, cont. O_2 purging and stirring, irradiation time = 70 min.

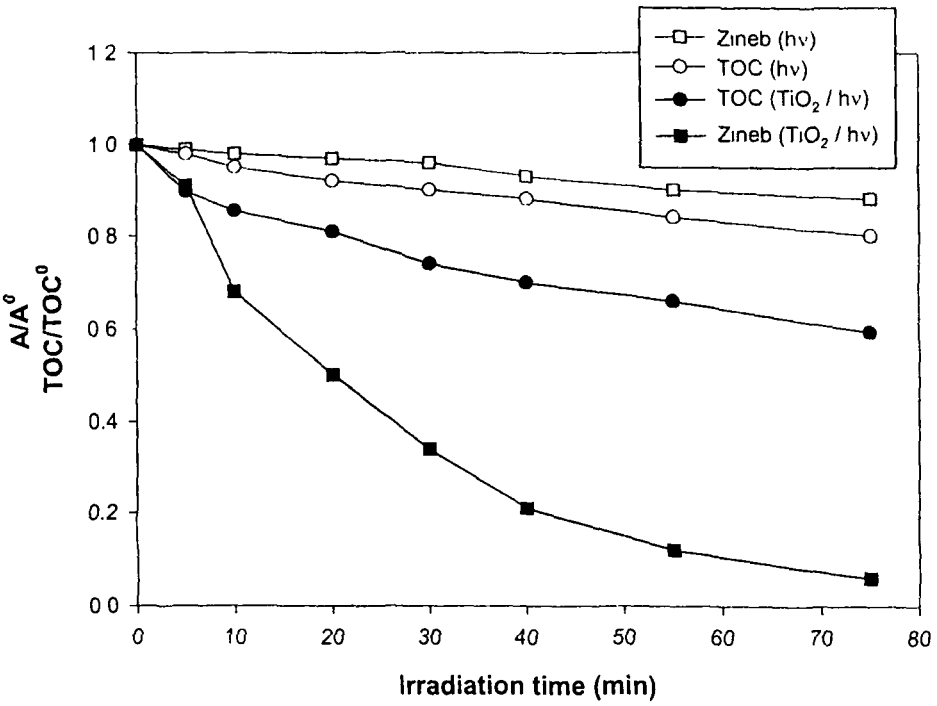


Figure 2.3. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of zineb (**3**) in the presence and absence of photocatalyst.

Experimental conditions: 0.8 mM zinb, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 277 nm, cont. O_2 purging and stirring, irradiation time = 75 min.

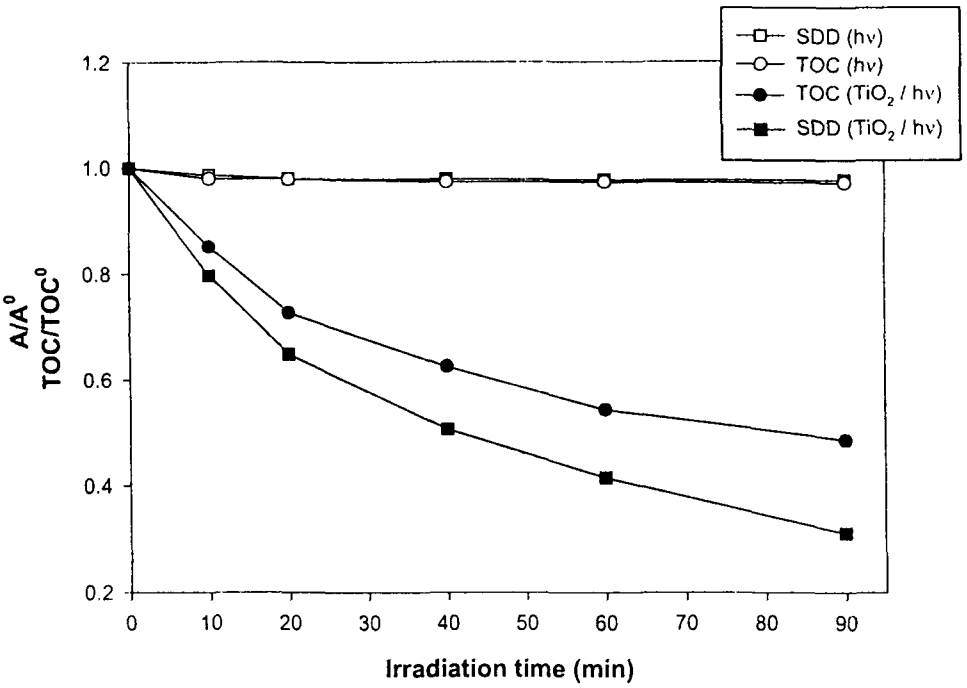


Figure 2.4. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of sodium dietyldithiocarbamate (SDD, **4**) in the presence and absence of photocatalyst.

Experimental conditions: 0.5 mM SDD, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 242 nm, cont. O_2 purging and stirring, irradiation time = 90 min.

could be seen from the figure that no observable loss of the compound take place when the irradiation was carried out in absence of photocatalyst.

Both the curves, decomposition (change in absorption intensity Vs irradiation time) and mineralization (change in TOC content Vs irradiation time) for the compounds under investigation can be fitted reasonably well by an exponential decay curve suggesting the first order kinetics. For each experiment, the degradation rate constant of the pesticide was calculated from the plot of the natural logarithm of the TOC and the absorbance of the pesticides as a function of irradiation time. The degradation rate for the mineralization and decomposition of the pesticide was calculated using formula given below,

$$\frac{-d[TOC]}{dt} = kc^{n} \qquad [1]$$

$$\frac{-d[A]}{dt} = kc^{n} \qquad [2]$$

TOC = Total Organic Carbon, A = absorbance, k = rate constant, c = concentration of the pollutant, n = order of reaction.

The degradation rate was calculated in terms of mole L^{-1} min^{-1}.

Control experiments were carried in all cases employing un-irradiated blank solutions. The zero irradiation time were obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

2.4.2 Comparison of the photocatalytic degradability of the pesticide derivatives (1-4)

Comparison of decomposition (change in absorption intensity Vs irradiation time) of pesticide derivative **1-4** (0.5 mM) on irradiation of an aqueous suspension with a 125 W medium pressure mercury lamp in the presence of TiO_2 (Degussa P25, $1gL^{-1}$) for 40 min is shown in Fig. **2.5**. It is interesting to note that the initial decomposition of the pesticide derivative zineb (**3**) is faster which slows down on prolonged irradiation time. The photodegradability of the four pesticide derivatives can then be ranked in the following order : Thiram $\geq$ Zineb > Carbaryl > Sodium diethyldithiocarbamate.

2.4.3 Comparison of different photocatalysts

The photocatalytic activity of four different commercially available TiO_2 powders (namely Degussa P25, Hombikat UV100, Milenium Inorganic PC500 and Travancore TTP) was tested on the degradation kinetics of the

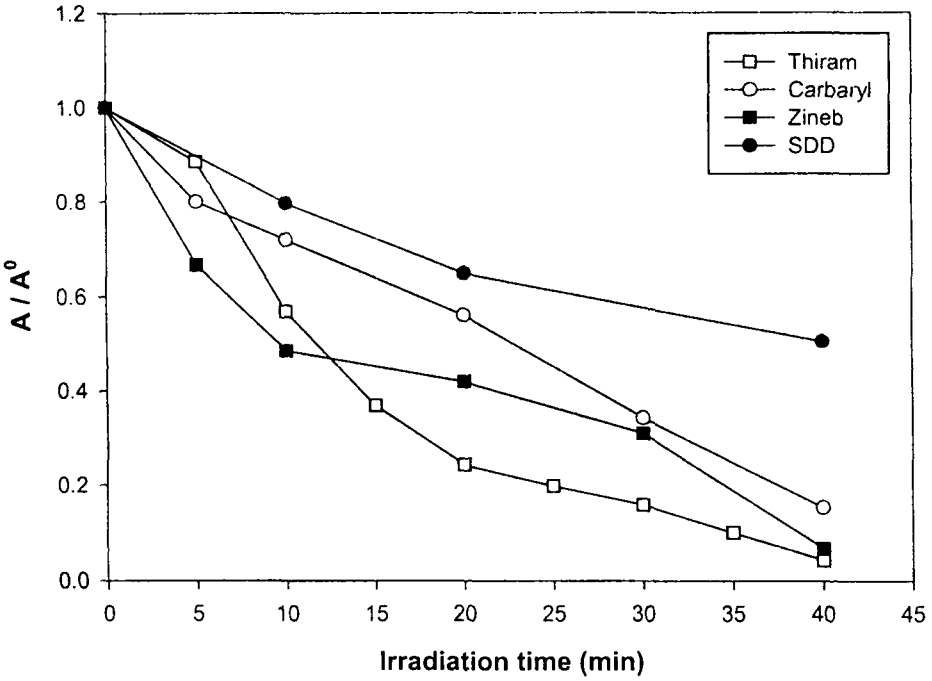


Figure 2.5. Comparison of decomposition (change in absorption intensity Vs irradiation time) of thiram (**1**), carbaryl (**2**) zineb (**3**) and sodium diethyldithiocarbamate (**4**, SDD).

Experimental conditions: pesticide concentration (**1-4**) 0.5 mM, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), light source 125 W medium pressure Hg lamp, immersion well photoreactor, cont. O_2 purging and stirring, irradiation time = 40 min.

pesticides under investigation. Fig. **2.6** shows the degradation rate for the decomposition of pesticide derivative **1**, whereas Figs. **2.7-2.9** show the degradation rate obtained for the decomposition and mineralization of the pesticide derivative **2-4**, respectively, in the presence of different types of TiO_2 powders. It has been observed that the degradation of all pesticides proceed much more rapidly in the presence of Degussa P25 as compared with other TiO_2 samples.

The reason for better photocatalytic activity of mixed phase titania photocatalyst Degussa P25 could be attributed on the basis that 1) the smaller band gap of rutile extends the usual range of photoactivity into the visible region. 2) the stabilization of charge separation by electron transfer from rutile to anatase slows the recombination. 3) the small size of the rutile crystallites facilitates the electron transfer.[17] In all following experiments, Degussa P25 was used as photocatalyst since this material exhibited the highest over all activity for the degradation of the pesticides.

2.4.4 pH Effect

The photodegradation of the pesticide derivatives, thiram (**1**) carbaryl (**2**) zineb (**3**) and sodium diethyldithiocarbamate (**4**) was investigated at different pH values, which is one of the most important

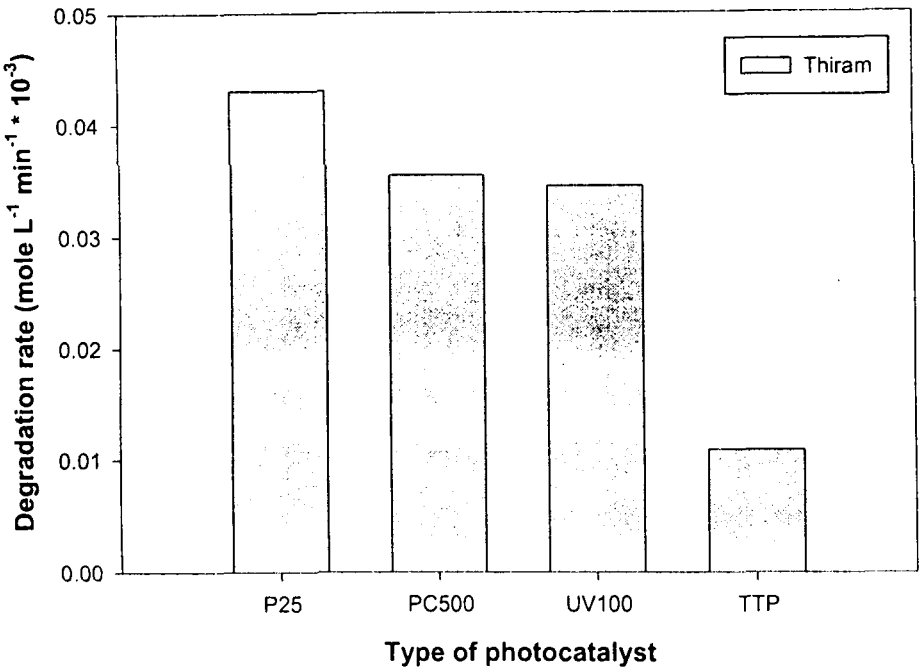


Figure 2.6. Comparison of degradation rate for the decomposition (change in absorption intensity Vs irradiation time) of thiram (**1**) in the presence of different photocatalysts.

Experimental conditions: 0.5 mM thiram, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), irradiation time 45 min.

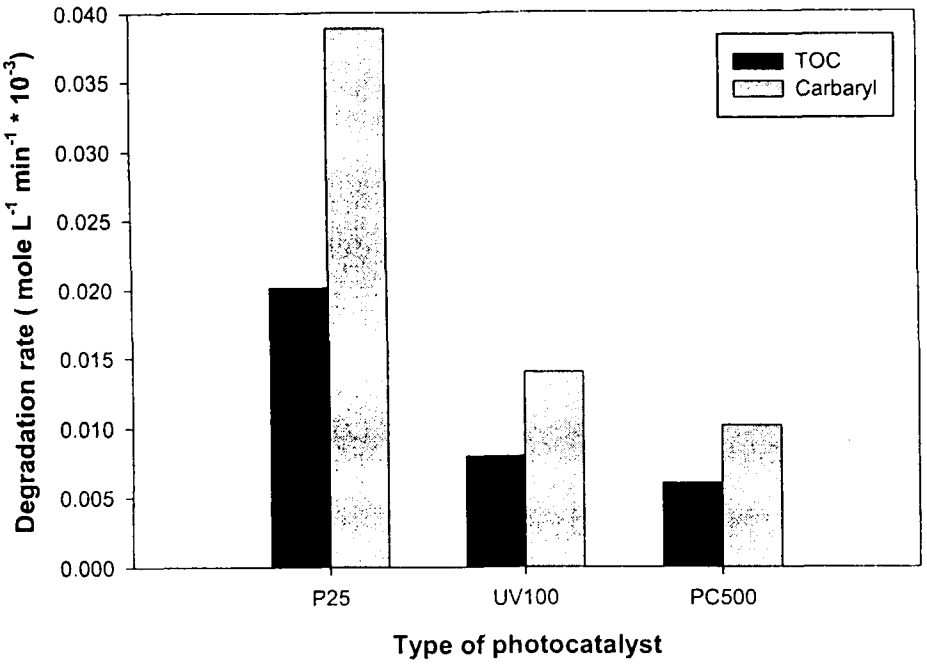


Figure 2.7. Comparison of degradation rate for the mineralization (TOC depletion Vs irradiation time) and for the decomposition (change in absorption intensity Vs irradiation time) of carbaryl (**2**) in the presence of different photocatalysts.

Experimental conditions: 0.5 mM carbaryl, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), irradiation time = 70 min.

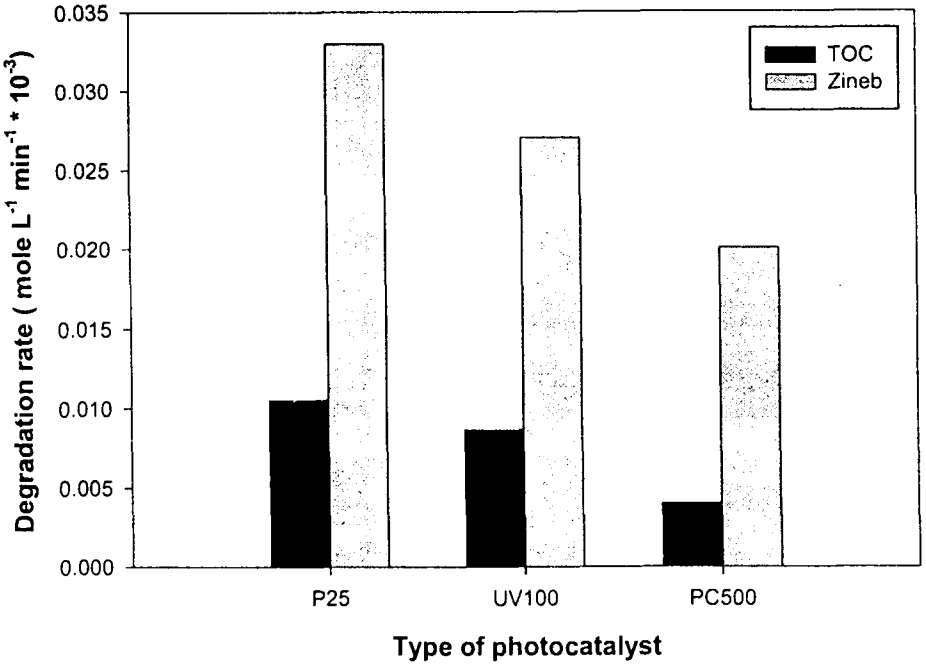


Figure 2.8. Comparison of degradation rate for the mineralization (TOC depletion Vs irradiation time) and for the decomposition (change in absorption intensity Vs irradiation time) of zineb (**3**) in the presence of different photocatalysts.

Experimental conditions: 0.8 mM zineb, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), irradiation time = 75 min.

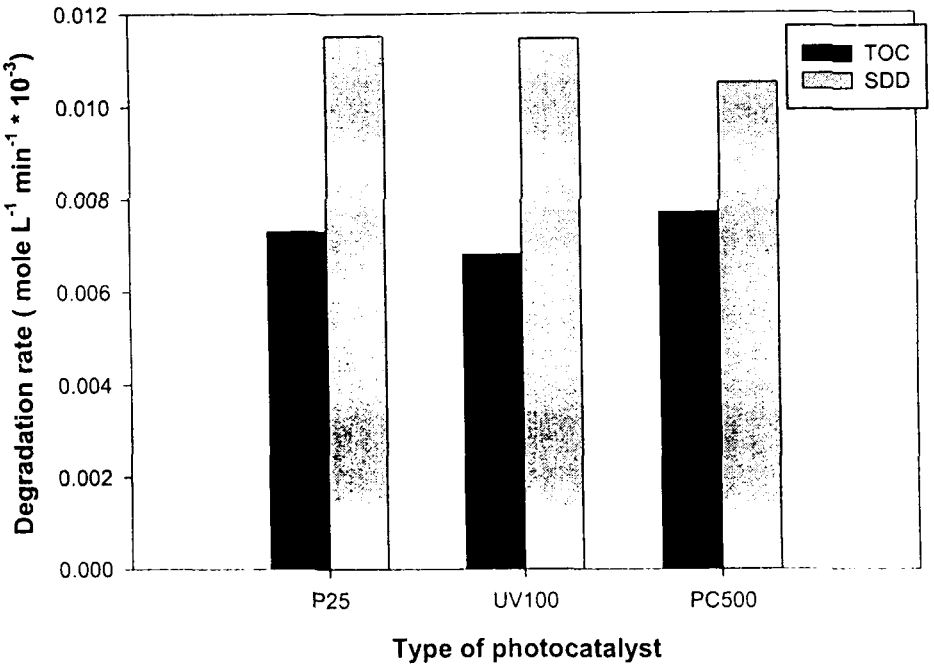


Figure 2.9. Comparison of degradation rate for the mineralization (TOC depletion Vs irradiation time) and for the decomposition (change in absorption intensity Vs irradiation time) of sodium diethyl dithiocarbamate (SDD, **4**) in the presence of different photocatalysts. Experimental conditions: 0.5 mM SDD, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), irradiation time = 90 min.

parameter in heterogeneous photocatalysis, since it influences the surface charge properties of the photocatalyst and therefore the adsorption behavior of the pollutants.[18,19]

Employing Degussa P25 as photocatalyst the decomposition and mineralization of the pesticide derivatives in the aqueous suspension of TiO_2 was studied under varying pH values. The degradation rate for the decomposition of the pesticide derivative **1** as a function of reaction pH is shown in Fig. **2.10**. The efficiency of degradation was found to be highest at pH 4 whereas lower and more or less similar rates were observed at pH 6.3, 8.4 and 9.8.

The degradation rate for the TOC depletion and decomposition of carbaryl (**2**), zineb (**3**) and sodium diethyldithiocarbamate (**4**) is shown in Figs. **2.11 - 2.13**, respectively. It has been observed that the degradation rate for the TOC depletion and decomposition of carbaryl (**2**) increases with the increase in pH from 4.6 to 6.2 and slight lower effecencies were observed at pH 8.4 and 9.6. In case of zineb (**3**) and sodium diethyldithiocarbamate (**4**) the rates were found to be better at lower pH, which decreases with increase in reaction pH. The better efficiency for the degradation of compounds at lower pH, may be due to the fact that the

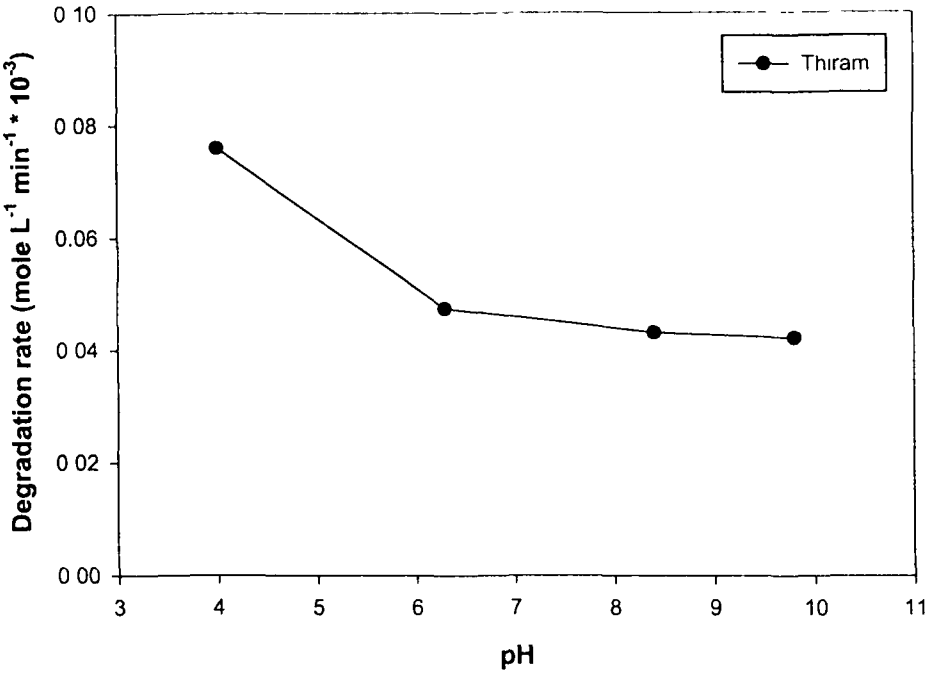


Figure 2.10. Influence of pH on the degradation rate for the decomposition of thiram (**1**).

Experimental conditions: 0.5 mM thiram, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (4.0, 6.3, 8.4 and 9.8), irradiation time = 45 min.

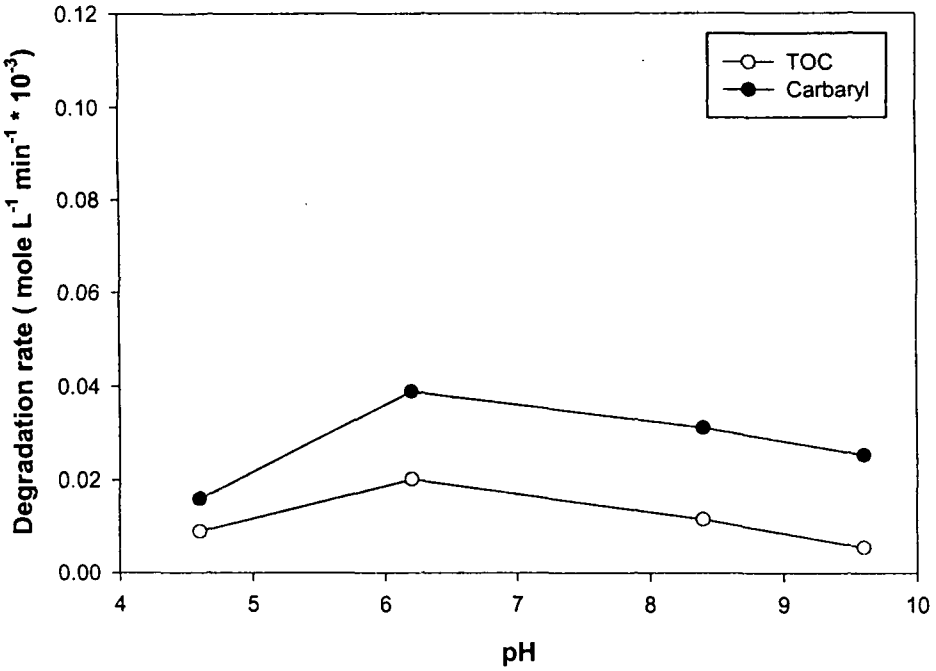


Figure 2.11. Influence of pH on the degradation rate for the mineralization and for the decomposition of carbaryl (**2**).

Experimental conditions: 0.5 mM carbaryl, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (4.6, 6.2, 8.4 and 9.6), irradiation time = 70 min.

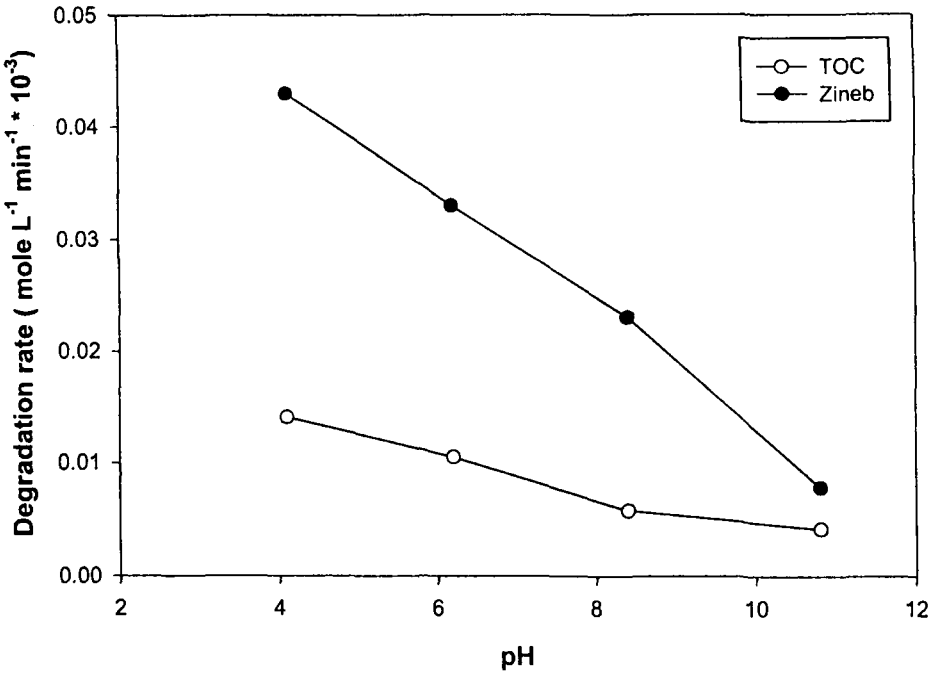


Figure 2.12. Influence of pH on the degradation rate for the mineralization and for the decomposition of zineb (**3**).

Experimental conditions: 0.8 mM zineb, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (4.1, 6.2, 8.4, and 10.8), irradiation time = 75 min.

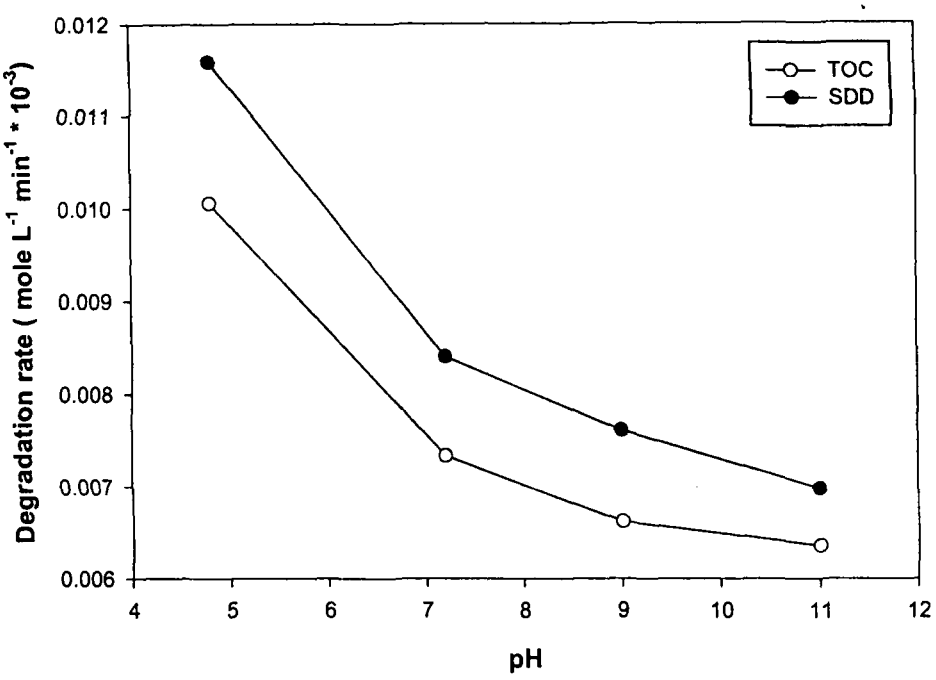


Figure 2.13. Influence of pH on the degradation rate for the mineralization and for the decomposition of sodium diethyldithiocarbamate (SDD, **4**).
Experimental conditions: 0.5 mM SDD, V=250 mL, photocatalyst TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (4.8, 7.2, 9.0 and 11.0), irradiation time = 90 min.

lone pairs of electrons present on the nitrogen atoms can be protonated and deprotonated under acidic and basic conditions. Apparently the photocatalytic oxidation seems to be favored in the structural orientation of the molecule, when it is protonated under lower pH values.

2.4.5 Effect of substrate concentration

Effect of substrate concentration on the degradation of the pesticide derivatives, thiram (**1**) carbaryl (**2**) zineb (**3**) and sodium diethyldithiocarbamate (**4**) was studied at different concentrations of the pesticide. The degradation rate for the decomposition of **1** as a function of substrate concentration employing Degussa P25 as photocatalyst is shown in Fig. **2.14**, where it has been found that the degradation rate increases with the increase in substrate concentration from 0.25 to 0.75 mM.

The degradation rate for the TOC depletion and for the decomposition of **2, 3** and **4** as a function of substrate concentration is shown in Figs. **2.15 - 2.17,** respectively. It is interesting to note that for the pesticide derivative **2**, the degradation rate for the decomposition increases rapidly with the increase in substrate concentration from 0.8 to 0.95 mM, whereas the depletion in TOC content slightly increases with the increase in substrate concentration from 0.5 to 0.95 mM. In case of

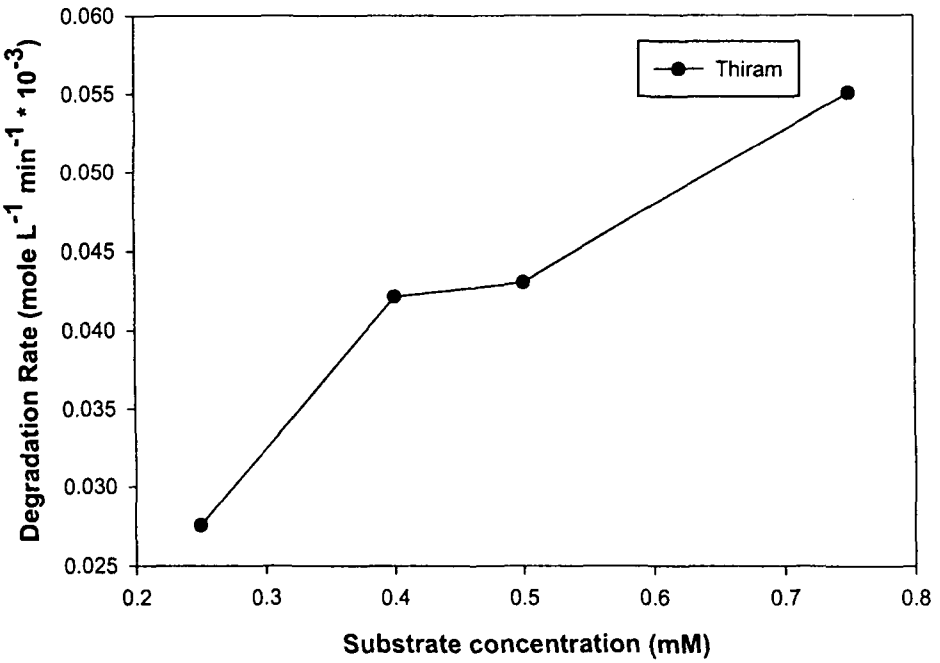


Figure 2.14. Influence of substrate concentration on the degradation rate for the decomposition of thiram (1). Experimental conditions: substrate concentrations (0.25, 0.40, 0.50 and 0.75 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 45 min.

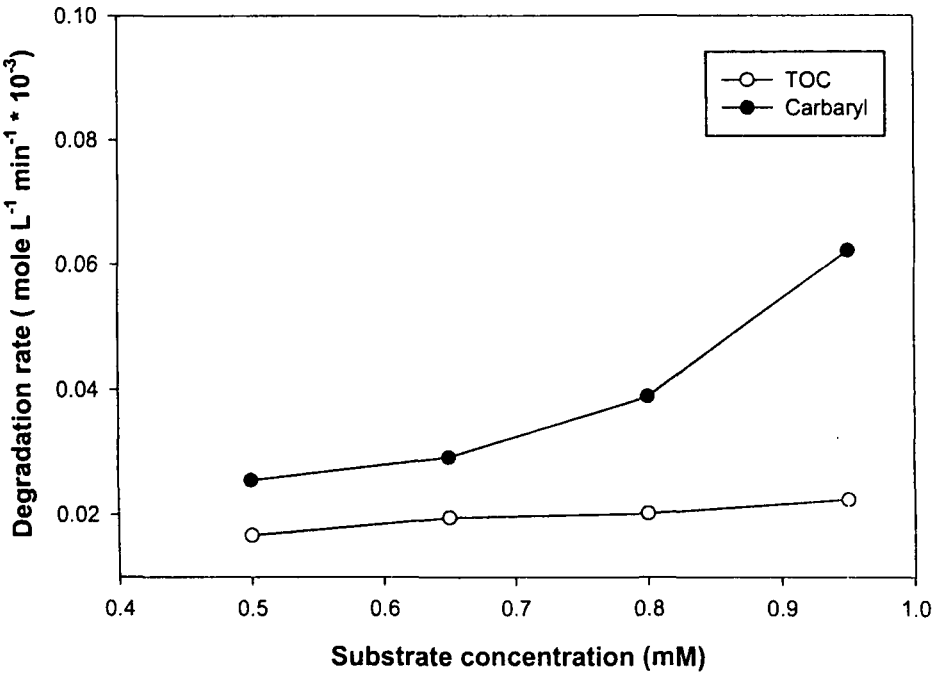


Figure 2.15. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of carbaryl (**2**).

Experimental conditions: substrate concentrations (0.5, 0.65, 0.80 and 0.95 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 70 min.

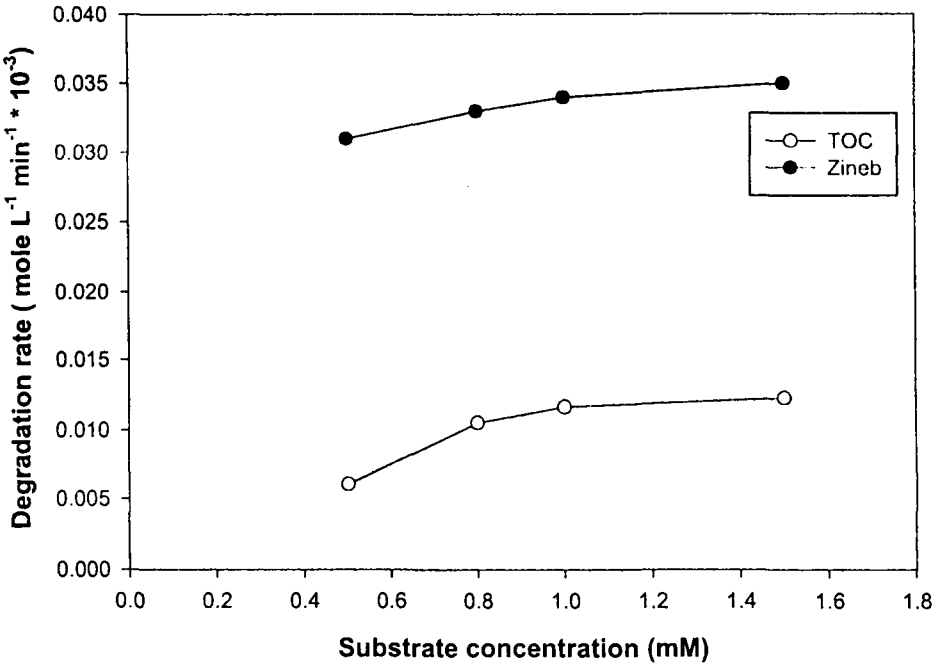


Figure 2.16. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of zineb (**3**).

Experimental conditions: substrate concentrations (0.5, 0.8, 1.0 and 1.5 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 75 min.

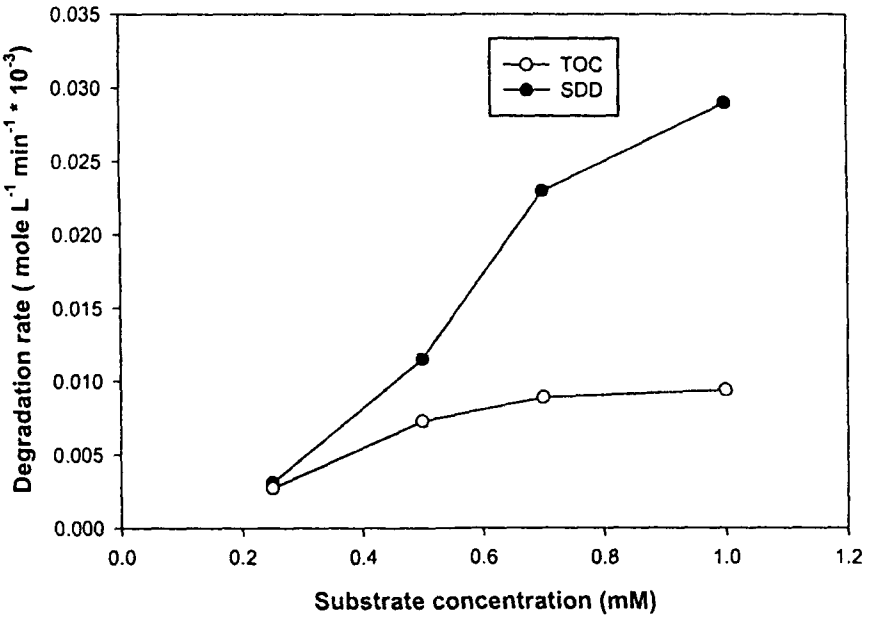


Figure 2.17. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of sodium diethyldithiocarbamate (SDD, **4**).

Experimental conditions: substrate concentrations (0.25, 0.50, 0.70 and 1.0 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 90 min.

pesticide derivates **3** and **4** the degradation rate increases with the increase in substrate concentration.

2.4.6 Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of pesticide derivatives, thiram (**1**) carbaryl (**2**) zineb (**3**) and sodium diethyldithiocarbamate (**4**) under investigation was studied employing different amounts of Degussa P25. The degradation rate for the decomposition of thiram (**1**) as function of different catalyst loading is shown in Fig. **2.18**. It is interesting to note that the degradation rate increases markedly on increasing the catalyst loading from 0.5 to 5 gL^{-1}.

The degradation rate for the TOC depletion and for the decomposition of **2, 3** and **4** as a function of catalyst concentration is shown in Figs. **2.19** - **2.21**, respectively. It has been found that the degradation rate of the pesticide derivatives **2-4** increases with the increase in catalyst loading from 0.5 to 3 gL^{-1}.

2.4.7 Effect of electron acceptors

The effect of electron acceptors such as Hydrogen peroxide, potassium bromate and ammonium persulphate in addition of molecular oxygen on the degradation kinetics of the pesticides derivatives **1-4** has

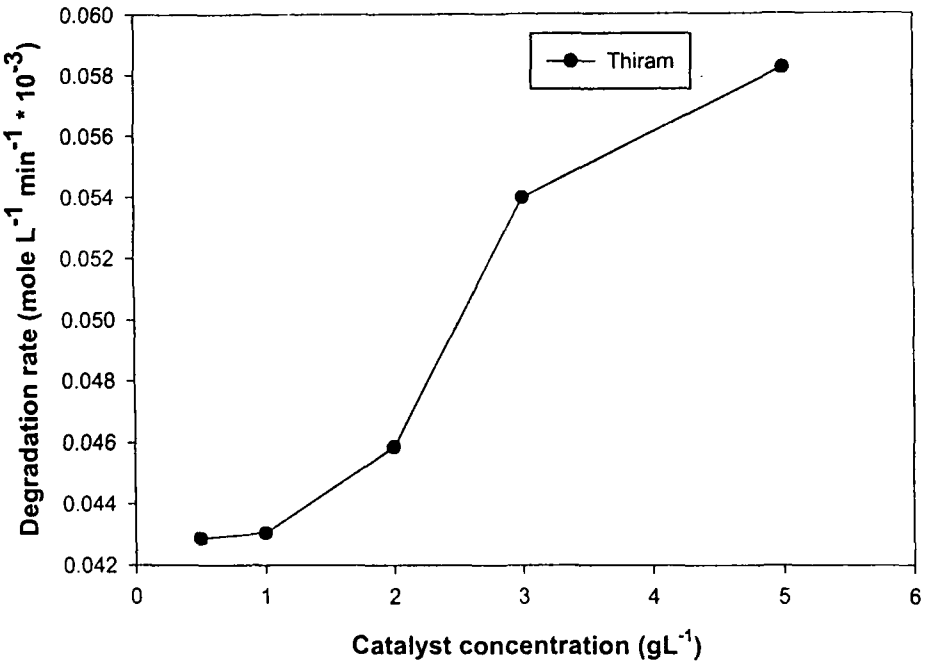


Figure 2.18. Influence of catalyst concentration on the degradation rate for the decomposition of thiram (**1**).

Experimental conditions: 0.5 mM thiram, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1.0, 2.0, 3.0 and 5.0 g L^{-1}), irradiation time = 45 min.

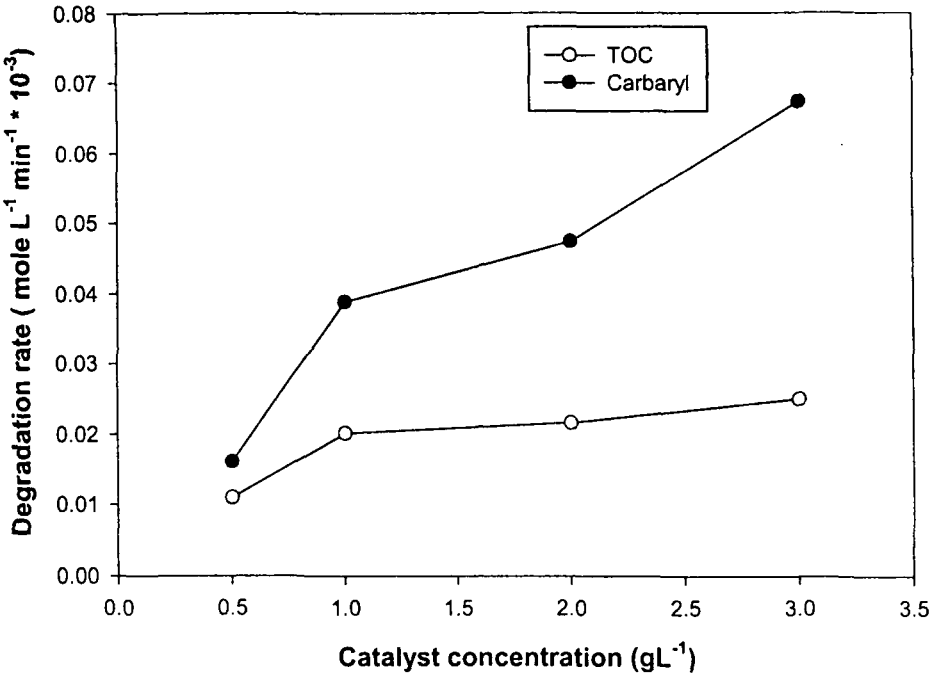


Figure 2.19. Influence of catalyst concentration on the degradation rate for the mineralization and for the decomposition of carbaryl (**2**).

Experimental conditions: 0.5 mM carbaryl, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1.0, 2.0 and 3.0 g L^{-1}), irradiation time = 70 min.

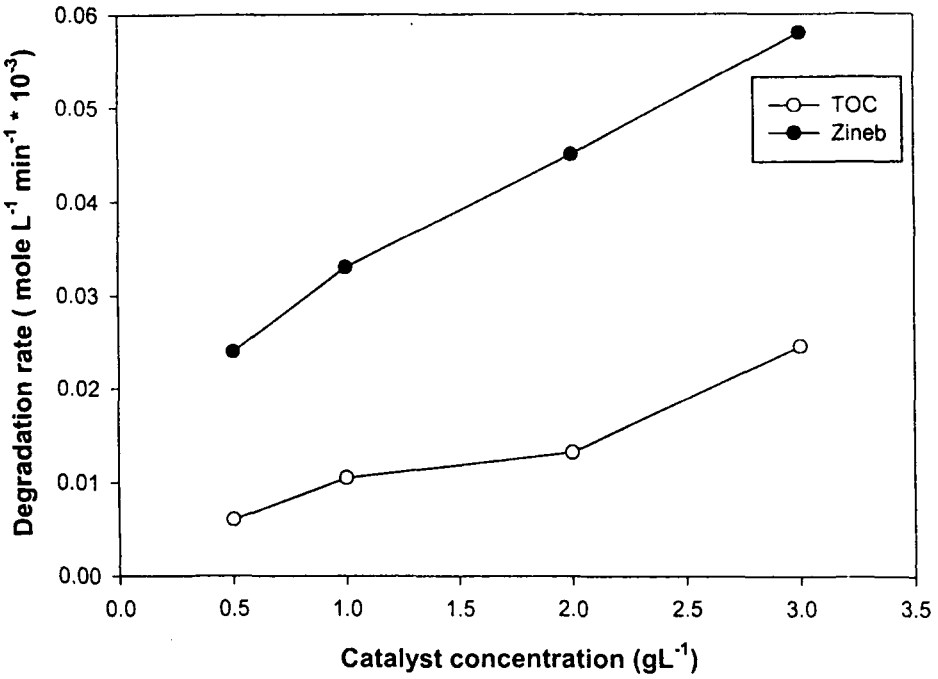


Figure 2.20. Influence of catalyst concentration on the degradation rate for the mineralization and for the decomposition of zineb (**3**).

Experimental conditions: 0.8 mM zineb, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1.0, 2.0 and 3.0 g L^{-1}), irradiation time = 75 min.

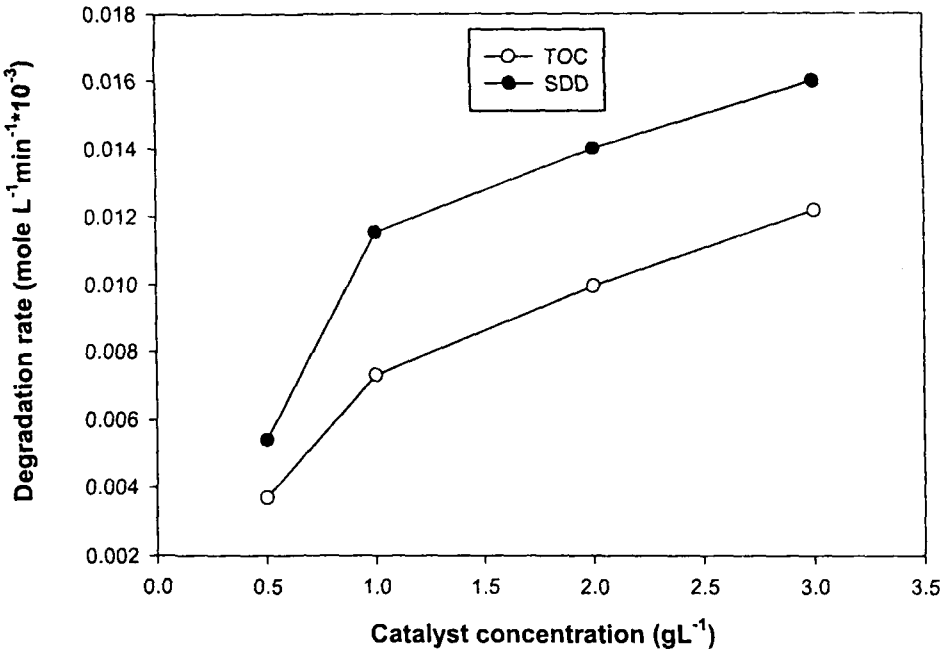


Figure 2.21. Influence of catalyst concentration on the degradation rate for the mineralization and decomposition of sodium diethyldithiocarbamate (SDD, **4**).

Experimental conditions: 0.5 mM SDD, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1.0, 2.0 and 3.0 g L^{-1}), irradiation time = 90 min.

been investigated in the presence of Degussa P25 as photocatalyst. Fig. **2.22** shows the degradation rate for decomposition of thiram (**1**) in the presence of electron acceptors such as hydrogen peroxide, potassium bromate and ammonium Persulphate containing Degussa P25 as photocatalyst. The addition of all the additives as electron acceptor has been found to enhance the degradation rate for the decomposition of the pesticide markedly as shown in the figure. Among all the additives, $KBrO_3$ shows the best degradation rate.

The degradation rate for the TOC depletion and decomposition of pesticide derivatives **2-4** in the presence of different electron acceptors is shown in Figs. **2.23 - 2.25**, respectively. For carbaryl (**2**), it could be seen from the Fig. **2.23** that the addition of hydrogen peroxide enhanced the degradation rate while other additive shows slight increase in degradation rate. It is interesting to note that for zineb (**3**), the degradation rate for the decomposition increases with the addition of additive but the mineralization rate is almost same within the experimental error. In sodium diethyldithiocarbamate (**4**), the degradation rate increases with the addition of electron acceptors. For the pesticide derivative **2-4**, hydrogen peroxide shows the beneficial effect for the degradation of the compounds as compare to other electron acceptors. Whereas in case of pesticide

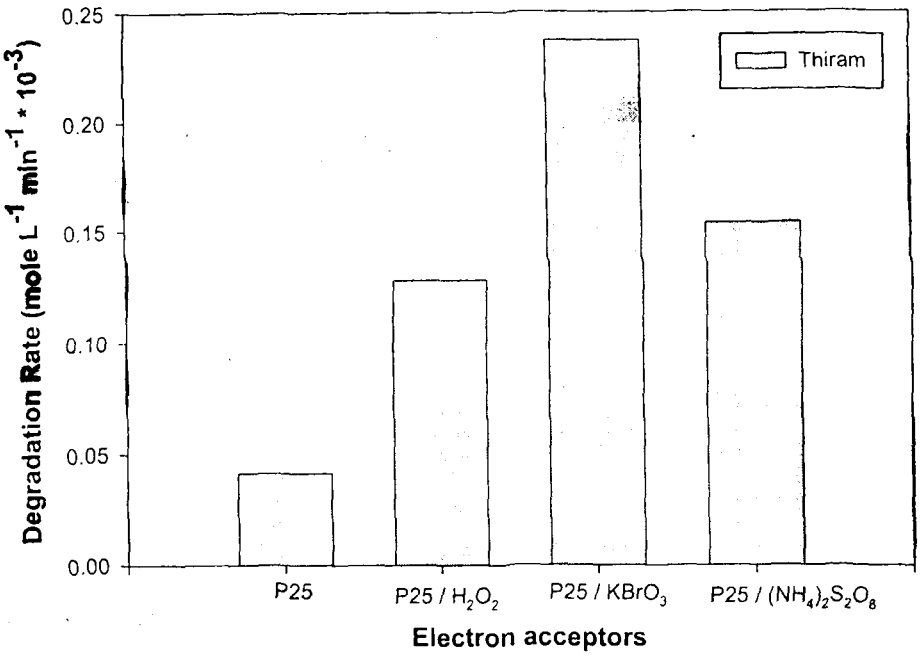


Figure 2.22. Comparison of degradation rate for the decomposition of thiram (1) in the presence of different electron acceptors.

Experimental conditions: 0.5 mM thiram, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 45 min.

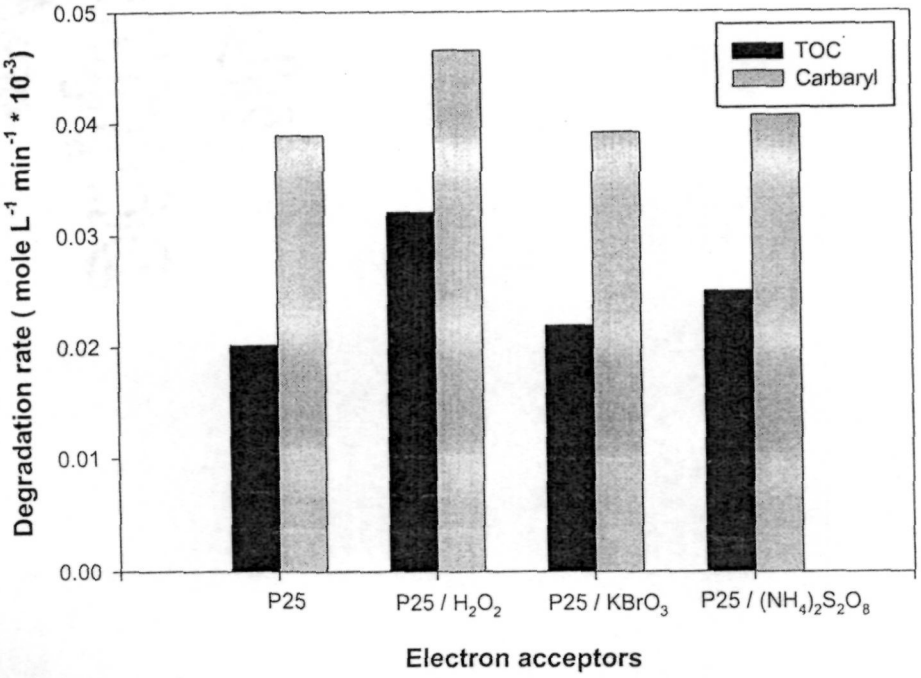


Figure 2.23. Comparison of degradation rate for the mineralization and for the decomposition of carbaryl (**2**) in the presence of different electron acceptors. Experimental conditions: 0.5 mM carbaryl, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 70 min.

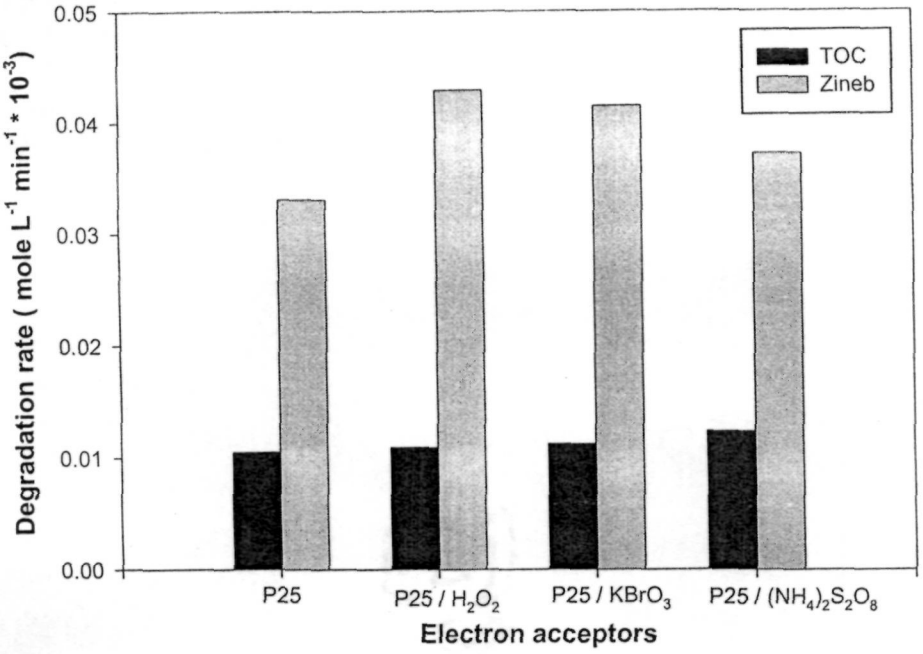


Figure 2.24. Comparison of degradation rate for the mineralization and for the decomposition of zineb (**3**) in the presence of different electron acceptors.
Experimental conditions: 0.8 mM zineb, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 75 min.

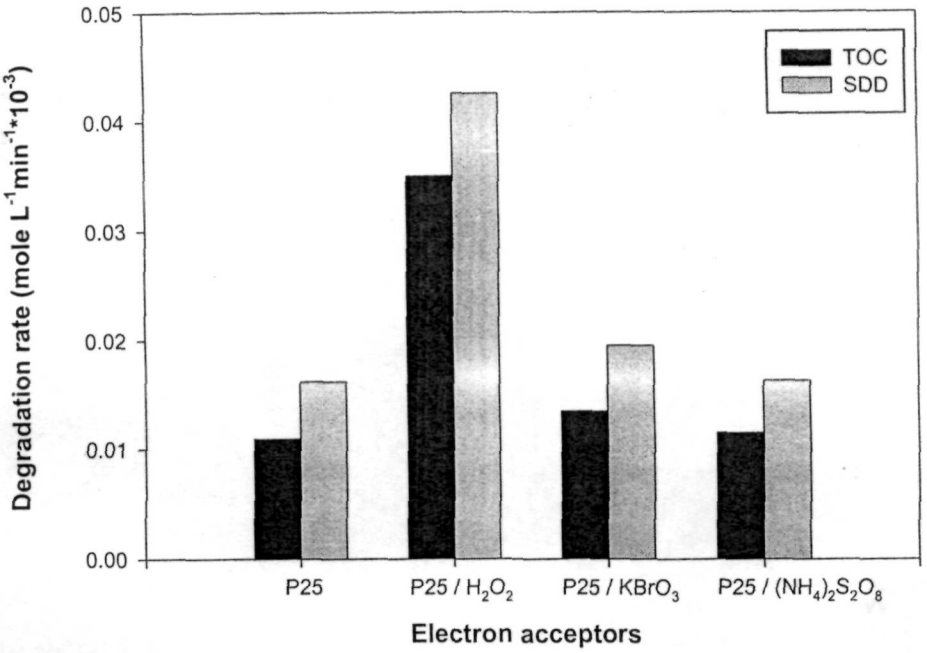


Figure 2.25. Comparison of degradation rate for the mineralization and for the decomposition of sodium diethyldithiocarbamate (SDD, **4**) in the presence of different electron acceptors.

Experimental conditions: 0.5 mM SDD, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 90 min.

derivative **1**, potassium bromate shows higher degradation rate as compare to other additives.

The effect of electron acceptors on the degradation of organic pollutants has already been discussed in chapter 1. As mentioned before, hydrogen peroxide and potassium bromate, generate reactive intermediate by the following eqns **1-3**.

$$H_2O_2 + e^-_{CB} \rightarrow \dot{O}H + OH^- \quad [1]$$

$$BrO_3^- + 2H^+ + e^-_{CB} \rightarrow BrO_2^{\bullet} + H_2O \quad [2]$$

$$BrO_3^- + 6H^+ + 6\ e^-_{CB} \rightarrow [BrO_2^-, HOBr] \rightarrow Br^- + 3H_2O \quad [3]$$

These reactive species may in turn either react with the pollutants or trap the photogenerated electron in the conduction band thereby reducing the back electron transfer. The net result leads to the enhancement of the degradation rate of the pollutants.

2.4.8 Photolysis of TiO_2 suspension containing thiram under sunlight

Wastewater treatment based on these processes, using sunlight is preferred from the application point of view. Hence the aqueous suspension of TiO_2 containing thiram was exposed to solar radiation. Fig. **2.26** shows the change in absorption intensity at 278 nm as a function of

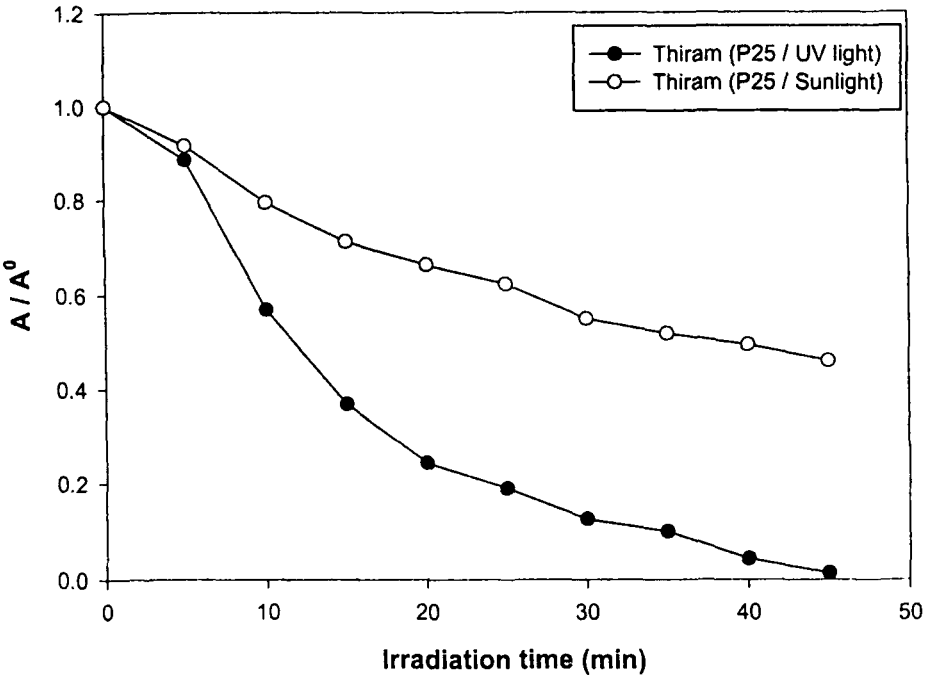


Figure 2.26. Change in absorption intensity at 278 nm as a function of irradiation time for an aqueous suspension of thiram (**1**) in the presence of photocatalyst under sunlight and UV light source.

Experimental conditions: a) UV Light: 0.5 mM thiram, V=250 mL, photocatalyst TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 45 min.

b) Sunlight: 0.5 mM thiram, V=250 mL, round bottom flask (250 mL), photocatalyst TiO_2 (Degussa P25, 1 gL^{-1}) cont. O_2 purging and stirring, irradiation time = 45 min.

irradiation time on illumination of an aqueous suspension of thiram (0.5 mM) in the presence of TiO_2 (P25, 1gL-1) under sunlight and UV light source. It was found that the degradation of the model compound proceeds much more rapidly in the presence of UV light source as compared to sunlight source.

2.4.9 Intermediate products

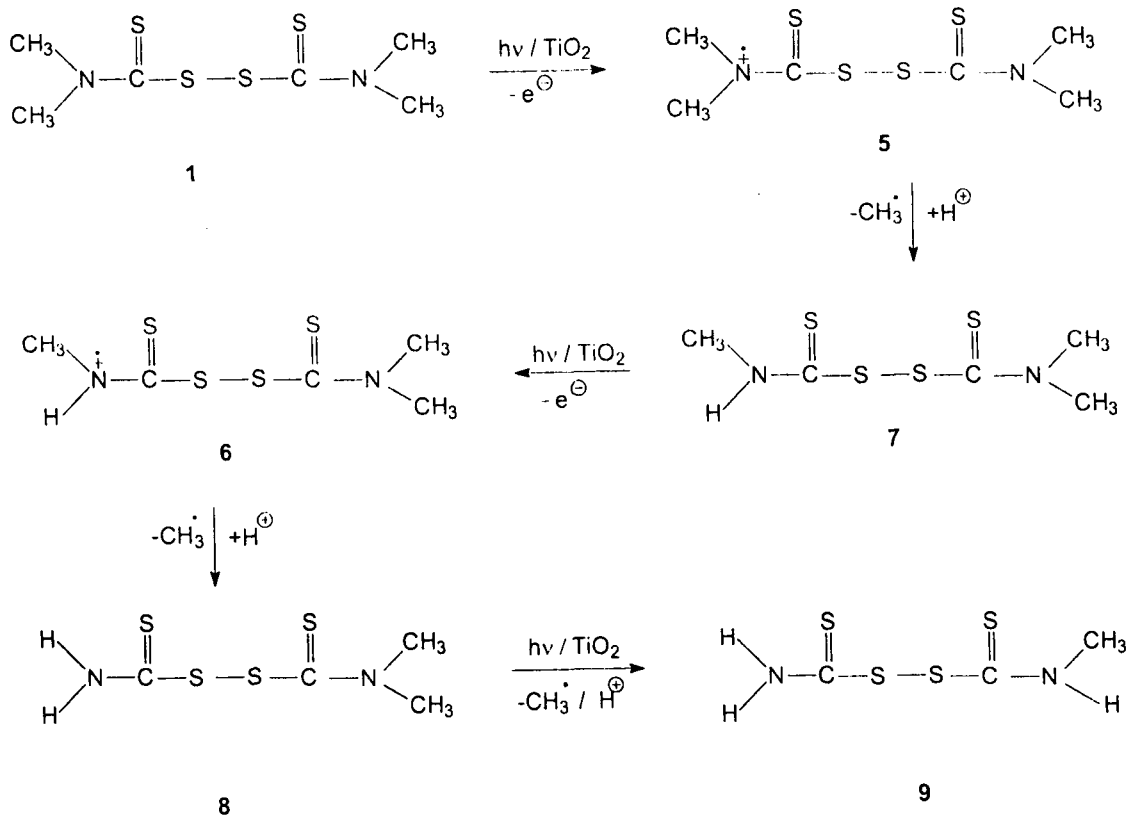
An attempt was made to identify the intermediate products formed in the photocatalytic degradation of all the pesticides, **1-4** in aqueous suspension of titanium dioxide through GC/MS analysis. An aqueous suspension of thiram (**1**, 0.5 mM, 250 mL) was irradiated in the presence of Degussa P25 (1 gL^{-1}) for 60 min with a 125W medium pressure mercury lamp in an immersion well photochemical reactor. The photocatalyst was removed by filtration and the solution was extracted in chloroform. The removal of the solvent under reduced pressure gave a residual mass, which was analyzed by GC/MS. The GC/MS analysis showed the formation of three products **7**, **8** and **11** appearing at retention times (t_R) 8.07, 6.92 and 10.06 min, respectively. The product was identified based on their molecular ion and mass spectrometric fragmentation peaks, as shown below;

Compound 7: m/z: 226 (M+), 222, 197, 183, 169, 155, 141, 127, 113, 99, 85, 71 and 57.

Compound 8: m/z: 212 (M+), 169, 154, 140, 126, 113, 99, 85, 71, 57 and 46.

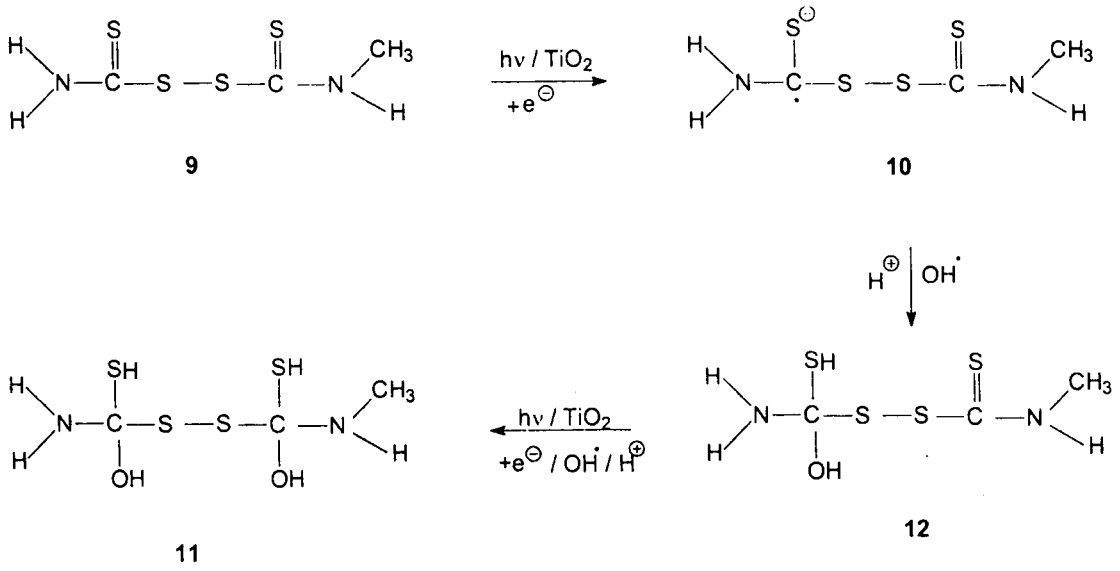
Compound 11: m/z: 234 (M+), 219, 203, 191, 185, 171, 149, 143, 129, 115, 102, 85, 73, 57 and 47.

The formation intermediate product **7** and **8** could be understood in terms of the pathway shown in Scheme **2.1**. While formation of **11** is explained in Scheme **2.2**. The model compound **1** upon the transfer of an electron can form the radical cation **5**, which may undergo loss of a methyl radical followed by abstraction of a proton to give **7**, which may subsequently undergo similar reaction leading to the formation of the observed product **8**. The formation of **11** could similarly be understood in terms of the pathways shown in Scheme **2.2**. The product **9** upon the transfer of an electron can form the radical anion **10**, which may undergo addition of a hydroxyl radical forming the product **12**, which may subsequently undergo similar reaction leading to the formation of the observed product **11**.



1 5 7 6 8 9

Scheme 2.1



9 10 11 12

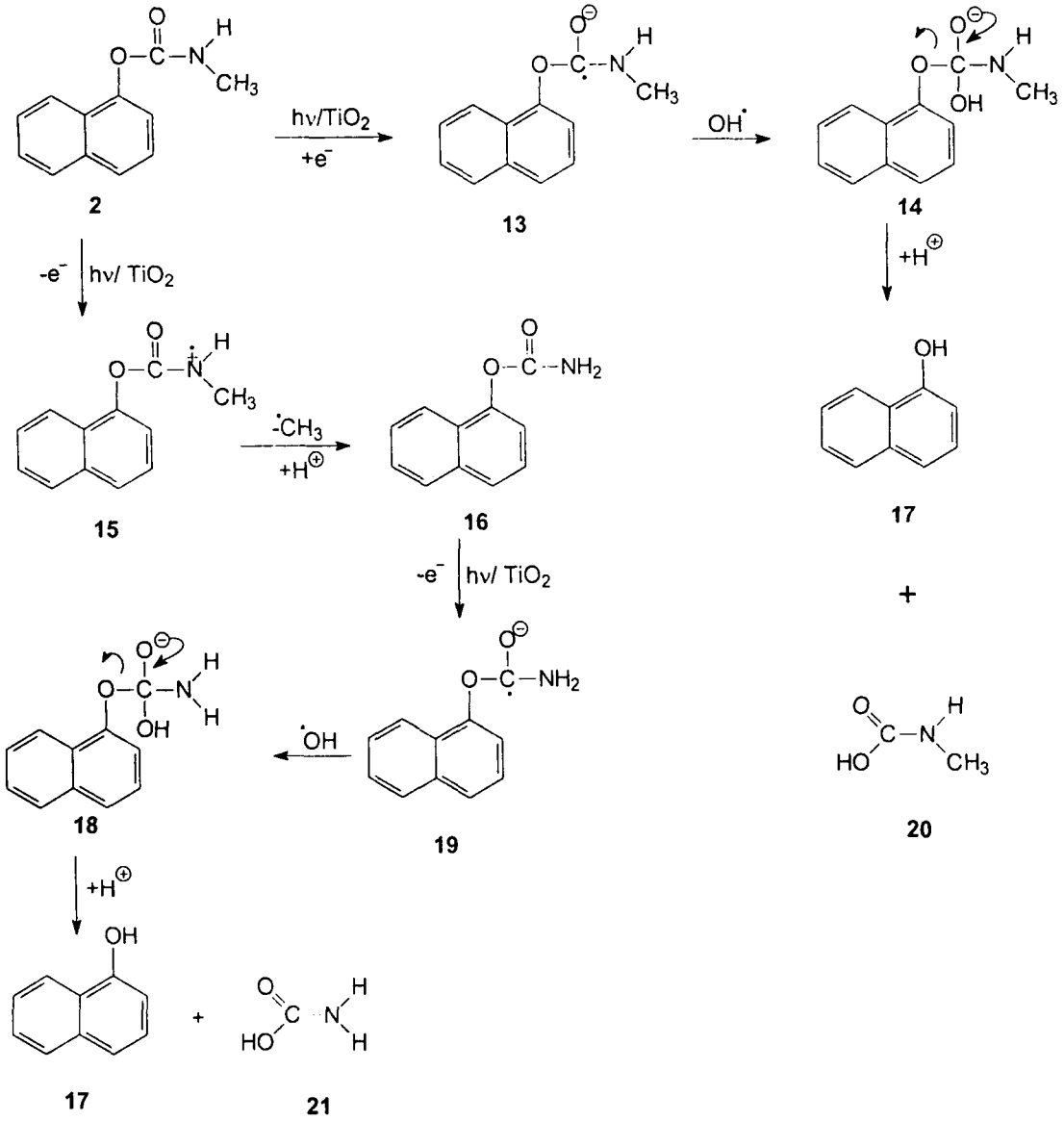
Scheme 2.1

Irradiation of an aqueous suspension of carbaryl (**2,** 0.25mM, 250 mL) and zineb (**3**, 0.20mM, 250 mL) in the presence of titanium dioxide (Degussa P25, $1gL^{-1}$) under analogous condition and workup of the reaction in usual manner gave a residual mass. GC/MS analysis of the irradiated residue showed the formation of several intermediate products. A probable pathway for the decomposition of **2** and **3** could be rationalized in terms of pathway shown in Scheme **2.3** and **2.4,** respectively.

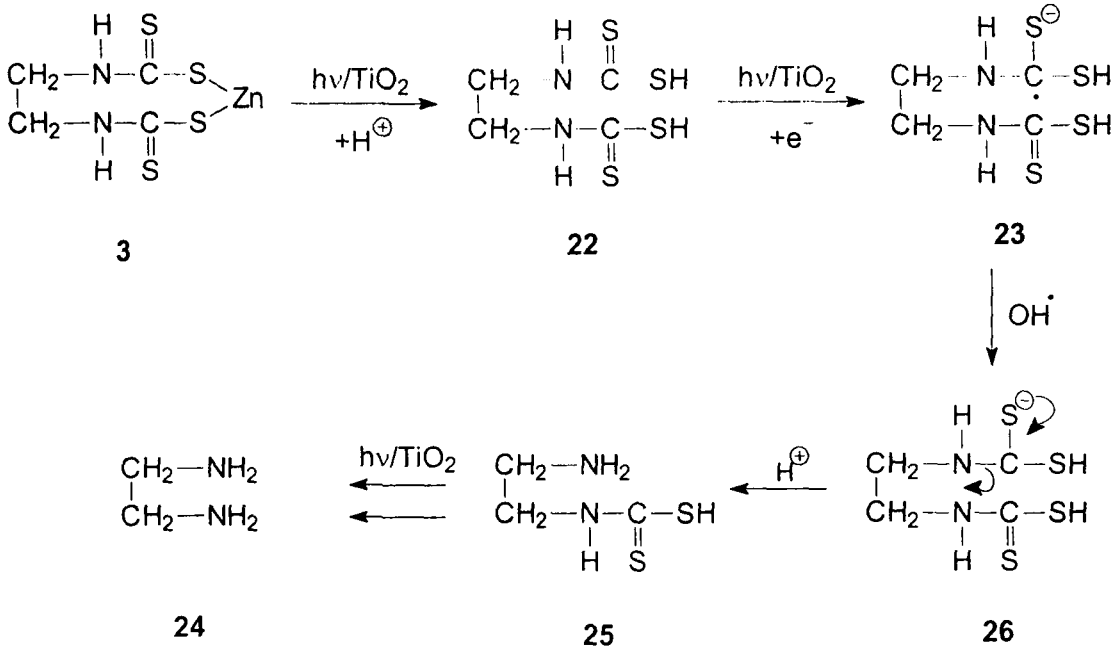
An aqueous suspension of sodium diethyldithiocarbamate (**4**, 0.5 mM, 250 mL) was irradiated in the presence of TiO_2 (Degussa P25, 1 gL^{-1}) under oxygen atmosphere with a 125W medium pressure mercury lamp in an immersion well photochemical reactor for 1 h. The photocatalyst was removed by filtration and the solution was extracted with chloroform. The removal of the solvent under reduced pressure gave a residual mass, which was analyzed by GC/MS. The GC/MS analysis showed the formation of two products **28** and **32** appearing at retention time (t_R) 4.666 min and 22.090, respectively. The product was identified based on their molecular ion and mass spectrometric fragmentation peaks, as shown below;

Compound 28: m/z : 167 (M^+), 149, 132, 113, 104, 83, 57 and 55.

Compound 32: m/z : 111 (M^+), 97, 83, 68, 55 and 47.

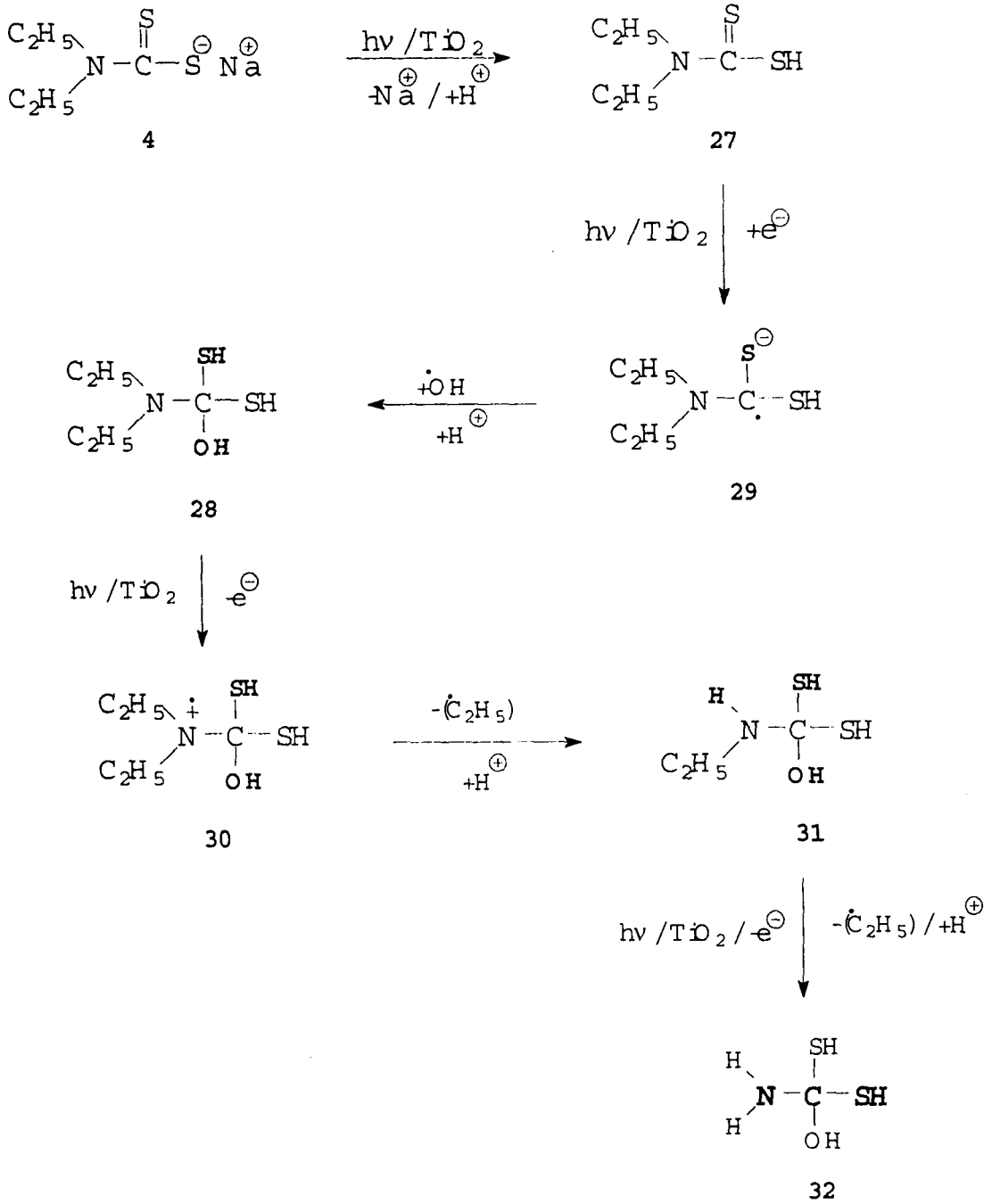

hν/TiO2
+e-
OH·
-e-
hν/ TiO2
·CH3
+H⊕
-e-
hν/ TiO2
·OH
+H⊕
+
2
13
14
15
16
17
18
19
20
17
21

Scheme 2.3



Scheme 2.4

A possible mechanism for the formation of intermediate products **28** and **32** could be understood in terms of pathway shown in Scheme **2.5**. The model compound **4**, on irradiated TiO_2 may undergo loss of sodium followed by the abstraction of proton to give **27**, which on addition of an electron can form a radical anionic species **29**. This species may undergo addition of a hydroxyl radical and a proton to give the observed product **28**. This product **28** may loose ethyl group through electron transfer reaction followed by the abstraction of proton to give the observed product **32**.



Scheme 2.5

References:

1 M. M. Haque and M. Muneer, *Ind. J. Chem. Tech.*, 12 (**2005**) 68.

2 M. M. Haque and M. Muneer, *Water Environ. Res.*, (communicated).

3 NIOSH (National Institute of Safety and Health), Registry of toxic effects of chemical substances (RTECS), **1986**.

4 U.S. Department of Agriculture, Soil conservation Service. SCS/ARS/CES Pesticide Properties Database, Version 2.0 (Summary), USDA-Soil Conservation Service, Syracuse, NY, **1990** (Nov).

5 J. Miyamoto, N. Mikami and Y. Takimoto, In Environmental fate of Pesticides, D. H. Huston, T. R. Roberts (Editors), Wiley: Chichester, UK, **1990**, p 123.

6 S.U. Khan, Pesticides in the Soil Environment, Elsevier, Amsterdam, **1980**, Chap. 5, p. 164.

7 E. Peris-Cardells, J. Tevol, A.R. Maurl, M. de la Guardia, Moliner and E. Pramauro, *J. Environ. Sci. Health B* 28 (4) (**1993**) 431.

8 E. Pramauro, A.B. Prevot, M. Vincenti and Brizzolesi, *Environ. Sci. Tecnol.*, 31 (**1997**) 3126.

9 V. Samanidou, K. Fytianos, G. Pfister and M. Bahadir, *Sci. Total. Environ.*, 76 (**1988**) 85.

10 G. Crank and A. Mursyidi, *J. Photochem. Photobiol. A:Chem.*, 68 (**1992**) 289.

11 K. Hasegawa, T. Kanbarra and S. Kagaya, *Denki Kagaku oyobi Kogyo Butsuri Kagaku,* 66 (**1998**) 625.

12 The photocatalyst Degussa P25 was a gift sample from Degussa-Huls, Frankfurt/Main, Germany.

13 The photocatalyst PC500 and Hombikat UV100 was a gift sample from Dr. D. W. Bahnemann from The Institut fuer Technische Chemie Universitat Hannover, Germany.

14 The photocatalyst TTP was obtained from Travancore Titanium Products, Kerala, India.

15 The Total Organic Carbon Analyzer was a gift equipment from the Alexander von Humboldt-Stiftung, Bonn, Germany.

16 GC/MS analysis was carried out from Sophisticated Instrumentation Center, Indian Institute of Technology, Powai, Mumbai, India.

17 D. C. Hurum, A. G. Agrios, K. A. Gray, T. Rajh and M. C. Thurnauer, *J. Phy. Chem. B,* 107 (**2003**) 4545.

18 J. Cunningham and G. Al-Sayyed, *J. Chem. Soc. Faraday Trans.*, 86 (**1990**) 3935.

19 J. Cunningham and P. Sedlak, *J. Photochem. Photobiol. A: Chem.*, 77 (**1994**) 255.

Chapter 3

PHOTOCATALYSED DEGRADATION OF TWO SELECTED SURFACTANTS, N,N-BIS(2-HYDROXYETHYL)DODECANOYL AMIDE AND CETYL TRIMETHYL AMMONIUM BROMIDE AND A TEXTILE DYE DERIVATIVE, BROMOTHYMOL BLUE IN AQUEOUS SUSPENSION OF SEMICONDUCTOR[1,2]

3.1 Abstract

The photocatalysed degradation of two selected surfactants, such as N,N-bis(2-hydroxyethyl)dodecanoyl amide (**1**) and cetyl trimethyl ammonium bromide (**2**) and a textile dye derivative, Bromothymol blue (**3**) have been investigated in aqueous suspensions of titanium dioxide under a variety of conditions such as different types of TiO_2, reaction pH, catalyst loading, substrate concentration, and in the presence of different electron acceptor besides molecular oxygen. The degradation of the pollutant was investigated by monitoring the change in substrate concentration employing UV spectroscopic analysis technique and depletion in TOC content as a function of irradiation time. The degradation rate for the decomposition and mineralization of the pollutant was found to be strongly influenced by all the above parameters. The photocatalyst, Degussa P25 was found to be more efficient for the degradation of all the model

compounds. The degradation products were analyzed by GC/MS analysis technique and probable pathways for the formation of products have been proposed.

3.2 Introduction

Numerous hazardous organic compounds are introduced into the environment through various sources. Among all the organic compounds, surfactants and dyes pose most serious problems in the environment. They cause serious ecological problem because most of them are difficult to degrade under standard biological methods.[3]

Various kinds of surfactants are employed in many fields, one pay little attention to their degradability. In particular, cationic surfactants, which are used in shampoos and rinses in large amounts, are difficult to biodegrade through bacteria. The demand and production of surfactants has been increased extensively.

Different types of dyes are used extensively in the textile industries such as reactive dyes, vat dyes, direct dyes, sulphur dyes, disperse dyes and naphthol dyes which are both water soluble and insoluble. In the process of dyeing a substantial amount of dyestuff is lost in textile industries[4], which pose a major problem for the industry as well as a threat to the environment.[5-9]

Therefore decolourization of dye effluents has acquired greater attention. During the past two decades, photocatalytic processes involving TiO_2 semiconductor particles under UV light illumination have been shown to be potentially advantageous and useful in the treatment of wastewater pollutants.

Apart from the mechanism proposed for the excitation of TiO_2 in the presence of O_2 and H_2O on illumination as indicated in chapter 1, there is a possibility of direct absorption of light by the dye which can lead to charge injection from exited state of the dye to the conduction band of the semiconductor as summarized in the following equations;

$$Dye_{ads} + hv \rightarrow Dye_{ads}^{*} \quad [1]$$

$$Dye_{ads}^{*} + TiO_2 \rightarrow Dye_{ads}^{\cdot +} + TiO_2\,(e^{-}) \quad [2]$$

It has been shown that heterogeneous photocatalytic oxidation processes can be used to remove colouring material from dye effluent in the presence of light.[10-27]

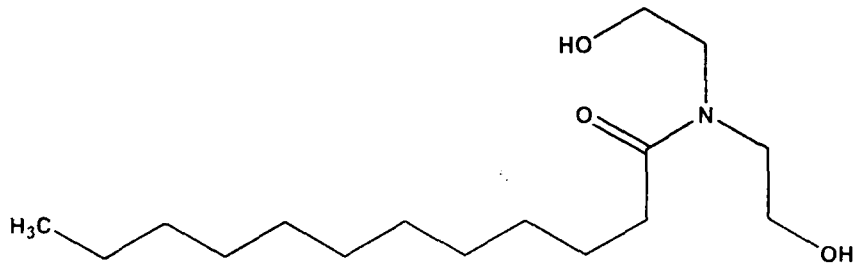
Photodegradation of wide variety of surfactants[28-33] in presence of TiO_2 has been reported earlier. Hidaka and coworkers have reported the photomineralization of a nonionic surfactant N,N-bis)2-hydroxyethyl)dodecanoyl amide[34] and cetyltrimethyl ammonium bromide[35] in presence of TiO_2. Photocatalytic degradation of textile dye bromothymol

blue using doped TiO_2 has also been investigated earlier[36]. No major effort has been made to study the detail degradation kinetics of these compounds under photocatalytic conditions, the knowledge of which is essential for the proper design of a treatment plant. Therefore, we have undertaken a detail study on the photodegradation of two selected surfactants, N,N-bis(2-hydroxyethyl)dodecanoyl amide (**1**) and cetyl trimethyl ammonium bromide (**2**) and a textile dye derivative bromothymol blue (**3**) (Chart **3.1**) sensitized by TiO_2 in aqueous solution under varying conditions. An attempt has also been made to identify the intermediate products formed during the photooxidation process of compound **1**, through GC/MS analysis technique.

3.3 Experimental

3.3.1 Reagent and chemicals

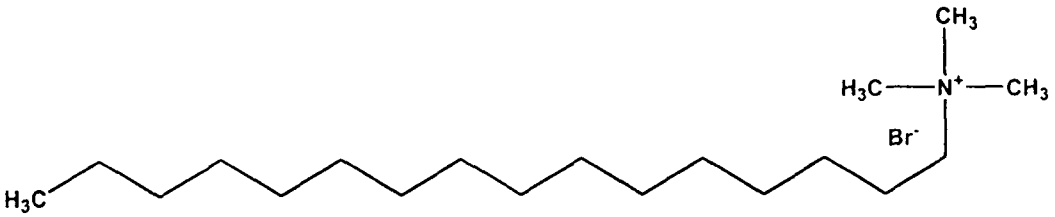
The surfactant, N,N-bis(2-hydroxyethyl)dodecanoyl amide (**1**) was a gift sample from Prof. Hisao Hidaka, Japan[37] and cetyl trimethyl ammonium bromide (**2**) was obtained from Qualigens Fine Chemicals, Bombay, India. The dye derivative, bromothymol blue (**3**) was obtained from Aldrich. These compounds were used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst, titanium dioxide samples such as Degussa P25 (Degussa AG),[38] Hombikat UV100 (Sachtleben chemie GmbH),[39] PC500 (Milenium



N,N-bis(2-hydroxyethyl)dodecanoyl amide

$C_{16}H_{33}NO_3$

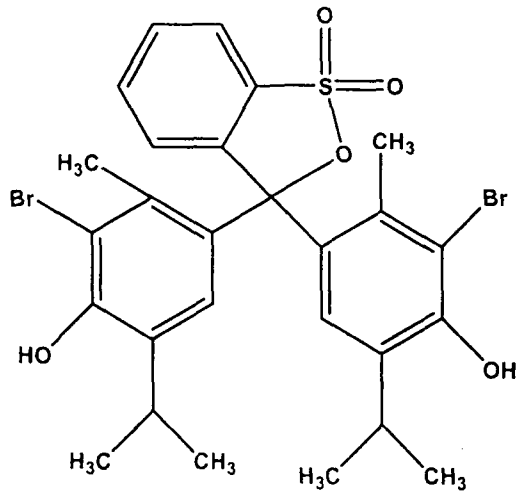
1



Cetyl trimethylammonium bromide

$C_{19}H_{42}BrN$

2



Bromothymol blue

$C_{27}H_{28}Br_2O_5S$

3

Chart 3.1 Chemical structure, name, and chemical formula.

inorganic chemicals)[39] and TTP (Travancore titanium products, India)[40] were used for the degradation studies. The other chemical used in this study such as NaOH, HNO_3, $(NH_4)_2S_2O_8$, H_2O_2 and $KBrO_3$ were obtained from Merck.

3.3.2 Procedure

For irradiation experiment the aqueous solution of the model compound with desired concentration was taken into the well immersion photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, water circulating jacket and an opening for supply of molecular oxygen. The required amount of photocatalyst was added and the solution was stirred and bubbled with molecular oxygen for at least 15 minutes in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (Philips). Samples (10 mL) were collected before and at regular intervals during irradiation and analysed after centrifugation.

3.3.3 Analysis

The degradation of N,N-bis(2-hydroxyethyl)dodecanoyl amide (**1**), cetyl trimethyl ammonium bromide (**2**) and bromothymol blue (**3**) was followed UV spectroscopically using Shimadzu UV-Vis Spectrophotometer (model 1601) by measuring the decrease in absorption intensity at their λ_{max} as function of irradiation time. The mineralization of these pollutants (**1-3**) under investigation was monitored by measuring the depletion in TOC as function of irradiation time using Shimadzu 5000 A TOC Analyzer.[41]

3.3.4 Characterization of intermediate photoproducts[42]

For the characterization of degradation product from the surfactant **1**, the aqueous solution (250ml) was taken in a photochemical reactor made of Pyrex glass and irradiated in presence of photocatalyst (Degussa P25, $1gL^{-1}$) for 120 minutes using 125 W medium pressure mercury lamp. The irradiated mixture was extracted with chloroform after removal of the photocatalyst, dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure to give a residual mass, which was analyzed by GC/MS analysis technique. For GC/MS analysis a Hewlett Packard Gas chromatograph and mass spectrometer (G1800 A) equipped with a 30 m HP-1 (d = 0.25 mm) capillary column, operating temperature

programmed (injection temperature 100 ^{0}C which is raised to 250 ^{0}C at the rate of 10 ^{0}C min^{-1} which is further raised to 280 ^{0}C at the rate of 30 ^{0}C min^{-1}) in splitless mode injection volume 0.5 μL with helium as a carrier gas was used.

3.4 Results and Discussion

3.4.1 Irradiation of an aqueous solution of N,N-bis(2-hydroxyethyl)dodecanoyl amide (1), cetyl trimethyl ammonium bromide (2) and bromothymol blue (3) in the presence of TiO_2

Irradiation of an aqueous solution of desired concentrations of N,N-bis(2-hydroxyethyl)dodecanoyl amide (**1**), cetyl trimethyl ammonium bromide (**2**) and bromothymol blue (**3**) in the presence of photocatalyst (TiO_2, 1 gL^{-1}) lead to decrease in adsorption intensity and depletion in TOC content as a function of time. The change in absorption intensity and depletion in TOC content Vs irradiation time in the presence and absence of the photocatalyst is shown in Figs. **3.1 - 3.3** for the photocatalytic degradation of compounds **1-3**, respectively. It could be seen from the figure that the loss of compound was negligible when the irradiation was carried out in absence of photocatalyst. The decomposition (change in absorption intensity Vs irradiation time) and mineralization (depletion in TOC content Vs irradiation time) curves of all the compounds under

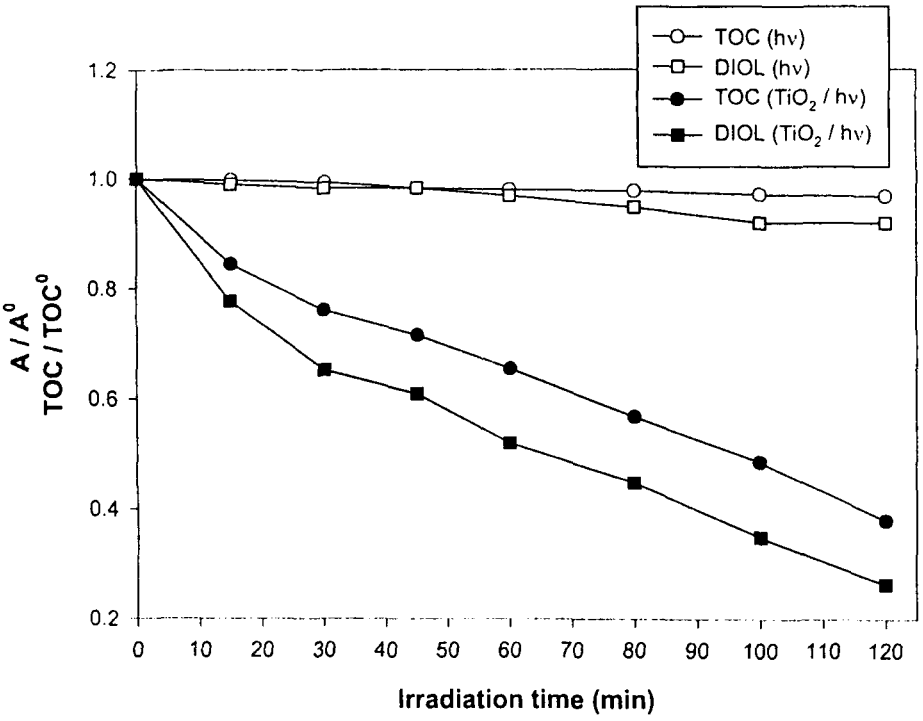


Figure 3.1. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of N,N-bis(2-hydroxyethyl)dodecanoyl amide (DIOL, 1) in the presence and absence of the photocatalyst.

Experimental conditions: 0.2 mM DIOL, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 202.5 nm, cont. O_2 purging and stirring, irradiation time = 120 min.

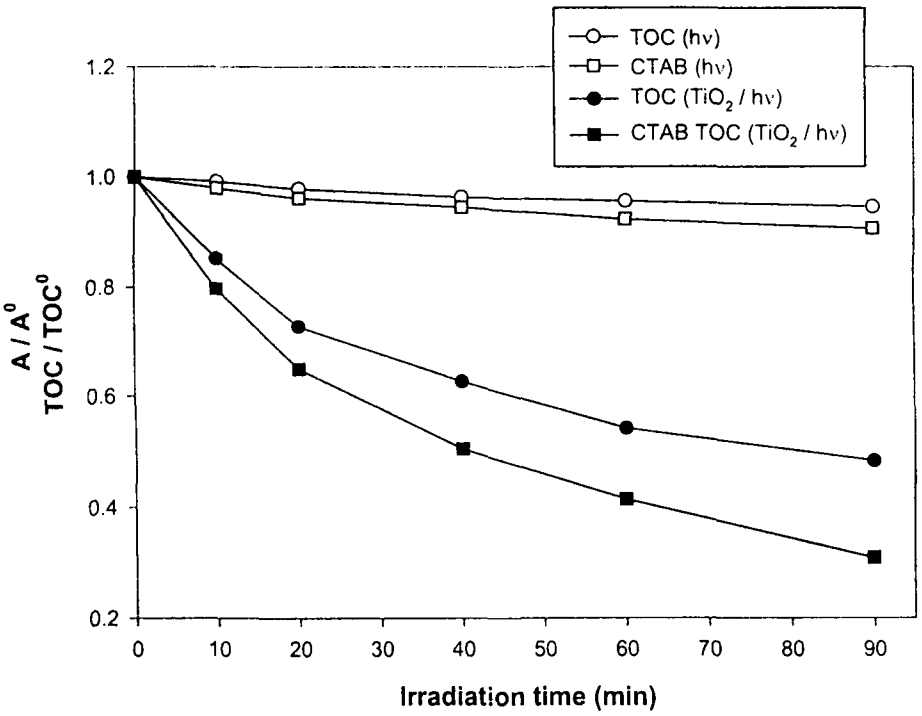


Figure 3.2. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of cetyl trimethyl ammonium bromide (CTAB, **2**) in the presence and absence of the photocatalyst.

Experimental conditions: 0.2 mM CTAB, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 243 nm, cont. O_2 purging and stirring, irradiation time = 90 min.

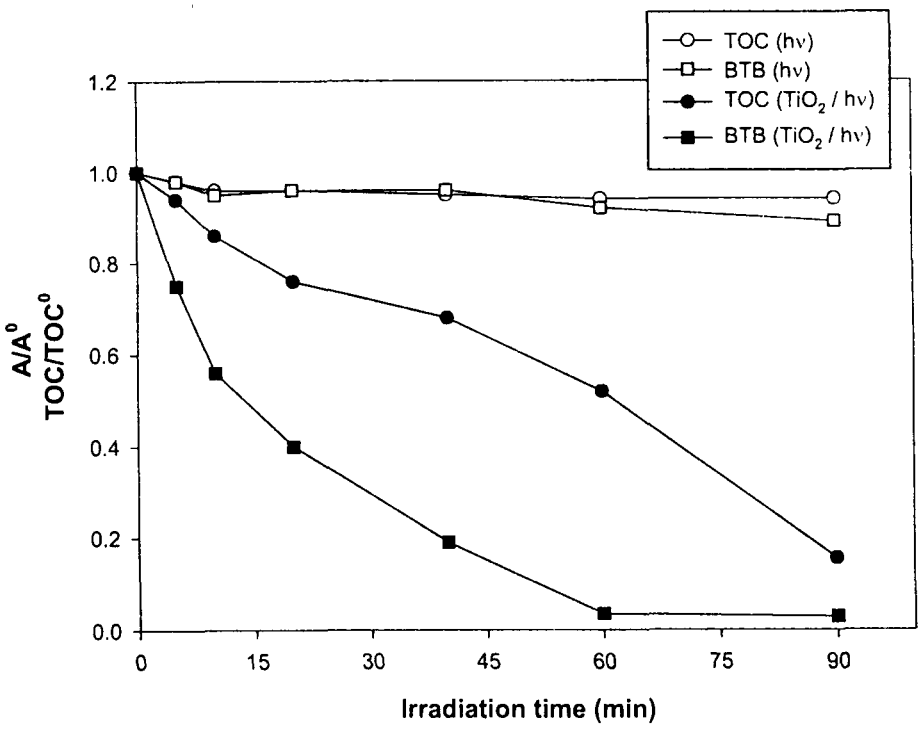


Figure 3.3. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of bromothymol blue (BTB, **3**) in the presence and absence of the photocatalyst.
Experimental conditions: 0.25 mM BTB, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 420 nm, cont. O_2 purging and stirring, irradiation time = 90 min.

investigation could be fitted reasonably well by an exponential decay curve suggesting first order degradation kinetics For each experiments, the rate constant was calculated from the plot of natural logarithm of TOC and the substrate concentration. The degradation rate for the mineralization and decomposition of the pollutants was calculated in terms of mole L^{-1} min^{-1}.

3.4.2 Comparison of the photocatalytic degradability of the surfactants 1 and 2

The comparison of change in absorption intensity and depletion in TOC as a function of time for the photocatalytic reaction of surfactants, N,N-bis(2-hydroxyethyl)dodecanoyl amide (**1**) and cetyl trimethyl ammonium bromide (**2**) is shown in Figs.**3.4** and **3.5**, respectively. The degradation of the surfactant **2** has found to be faster than the surfactant **1**.

3.4.3 Comparison of different photocatalysts

We have tested the photocatalytic activity of four different commercially available TiO_2 powders (namely Degussa P25, Hombikat UV100, PC500 and TTP) on the degradation kinetics of N,N-bis(2-hydroxyethyl)dodecanoyl amide (**1**), cetyl trimethyl ammonium bromide (**2**) and bromothymol blue (**3**). The degradation rate obtained for the TOC depletion and decomposition of compounds **1-3**, in the presence of different types of TiO_2 powders is shown in Figs. **3.6-3.8**, respectively. The

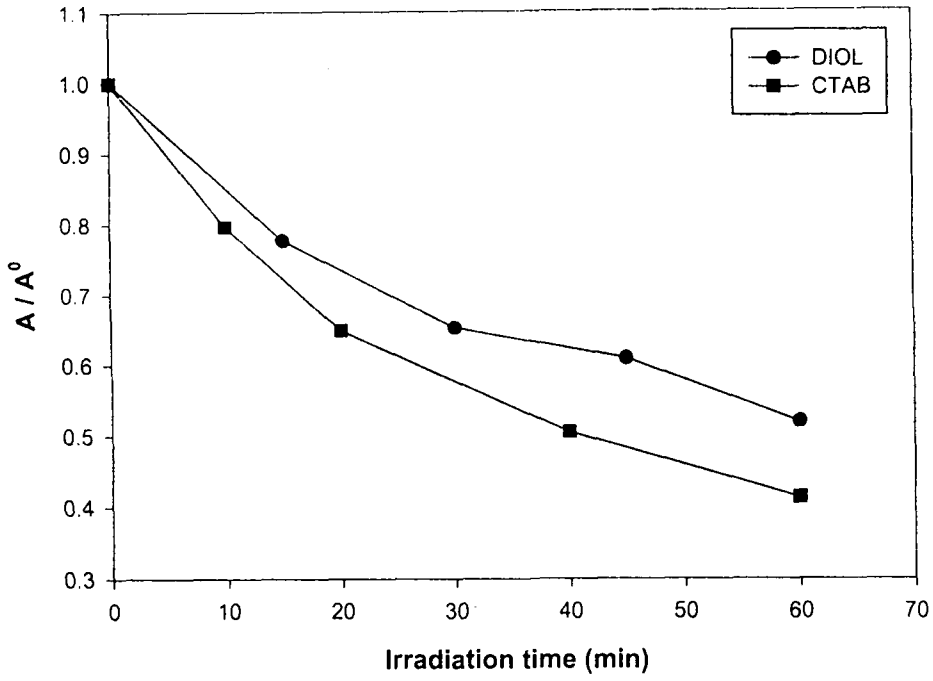


Figure 3.4. Comparison of change in absorption intensity as a function of time for the photocatalytic reaction of N,N-bis(2-hydroxyethyl)dodecanoyl amide (DIOL, **1**) and cetyltrimethyl ammonium bromide (**2**, CTAB).

Experimental conditions: surfactant concentration 0.2 mM, V=250 mL, photocatalyst: TiO_2 Degussa P25 (1 gL^{-1}), immersion photoreactor, light source: 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 60 min.

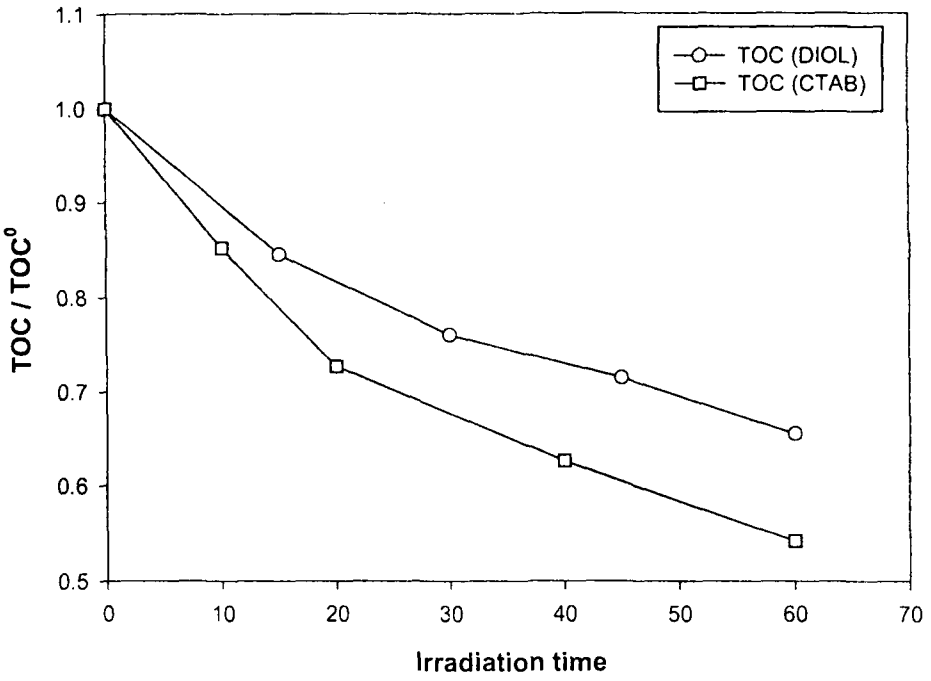


Figure 3.5. Comparison of TOC depletion as a function of time for the photocatalytic reaction of N,N-bis(2-hydroxyethyl)dodecanoyl amide (DIOL, **1**) and cetyltrimethyl ammonium bromide (**2**, CTAB).
Experimental conditions: surfactant concentration 0.2 mM, V=250 mL, photocatalyst: TiO_2 Degussa P25 (1 gL^{-1}), immersion photoreactor, light source: 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 60 min.

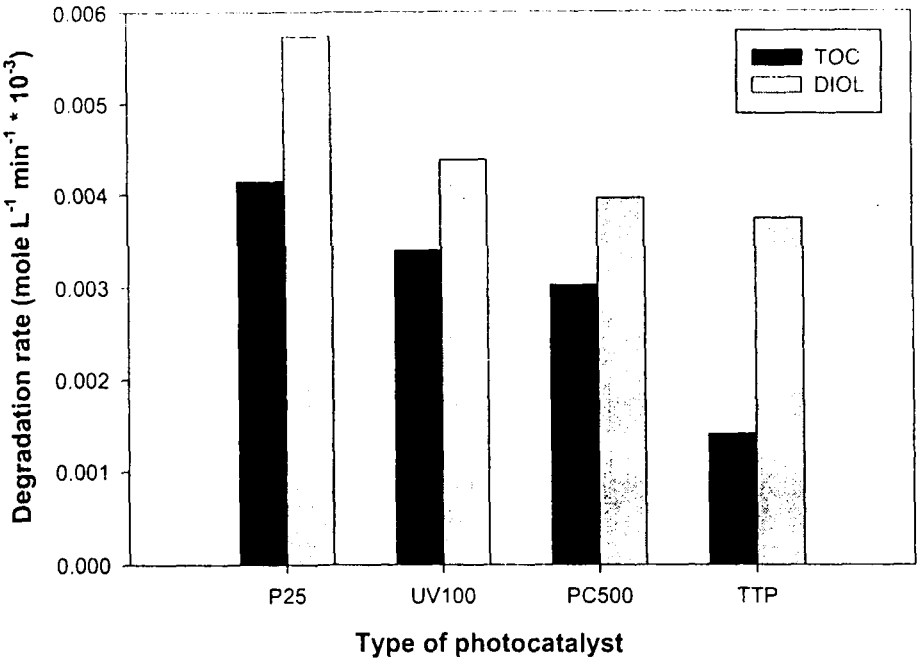


Figure 3.6. Comparison of degradation rate for the mineralization (TOC depletion Vs irradiation time) and for the decomposition (change in absorption intensity Vs irradiation time) of N,N-bis(2-hydroxyethyl)dodecanoyl amide (DIOL, **1**) in the presence of different photocatalysts.

Experimental conditions: 0.2 mM DIOL, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), TTP (1 gL^{-1}), irradiation time = 120 min.

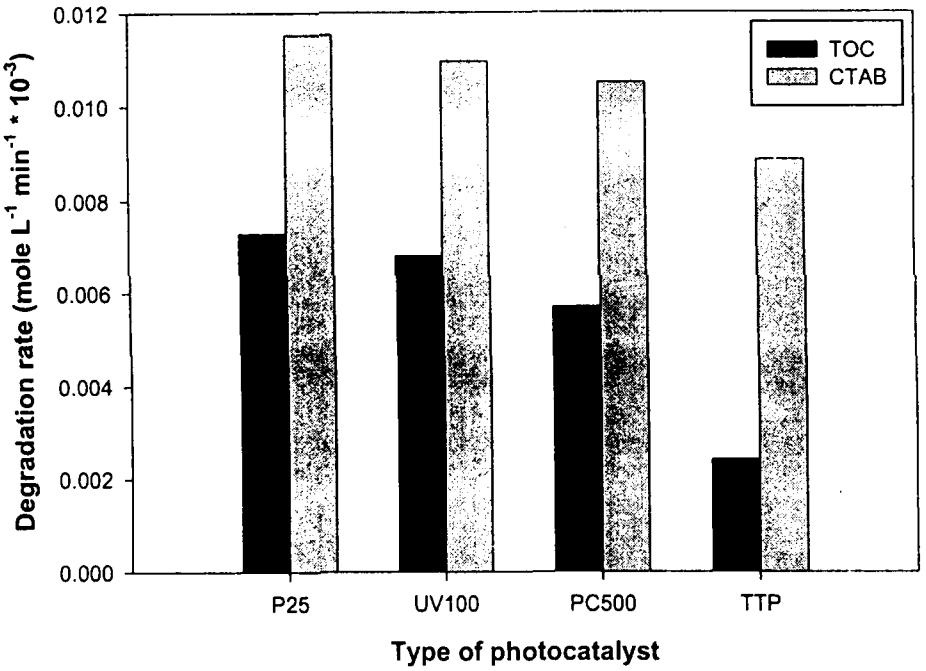


Figure 3.7. Comparison of degradation rate for the mineralization (TOC depletion Vs irradiation time) and for the decomposition (change in absorption intensity Vs irradiation time) of cetyl trimethyl ammonium bromide (CTAB, **2**) in the presence of different photocatalysts. Experimental conditions: 0.2 mM CTAB, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), TTP (1 gL^{-1}), irradiation time = 90 min.

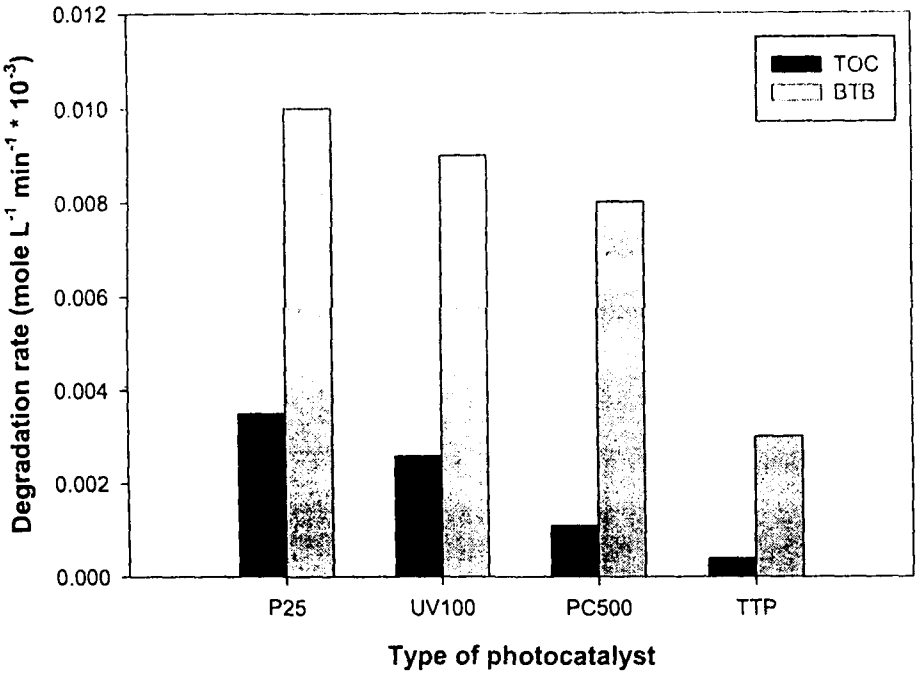


Figure 3.8. Comparison of degradation rate for the mineralization (TOC depletion Vs irradiation time) and for the decomposition (change in absorption intensity Vs irradiation time) of bromothymol blue (BTB, **3**) in the presence of different photocatalysts.

Experimental conditions: 0.25 mM BTB, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), TTP (1 gL^{-1}), irradiation time = 90 min.

degradation efficiency of all the compounds under investigation was found to be better in the presence of Degussa P25 as compared with other TiO_2 powders. Therefore, in all following experiments the photocatalyst Degussa P25 was used for the degradation experiments under different conditions.

The reason for better photocatalytic activity of Degussa P25 has already been discussed in chapter 1 and 2.

3.4.4 pH Effect

Employing Degussa P25 as photocatalyst the degradation of compounds **1-3** was studied in the pH range between 2 to 9. The degradation rate obtained for the decomposition and for the mineralization of compounds **1-3** as a function of reaction pH is shown in Figs. **3.9-3.11**, respectively. The degradation rate for the decomposition and for the mineralization of surfactants **1** and **2** was found to be better under acidic pH, which decreases with the increase in pH of the reaction mixture, whereas in case of dye derivative **3**, the rate was found to be more or less similar in the pH range studied within the experimental error limits.

It has been found that when the reaction of the dye derivative **3**, was carried out at pH 9.0, there was appearance of new absorption peak at 645 nm beside its λ_{max} of 420 nm as shown in Fig **3.12**. The absorption

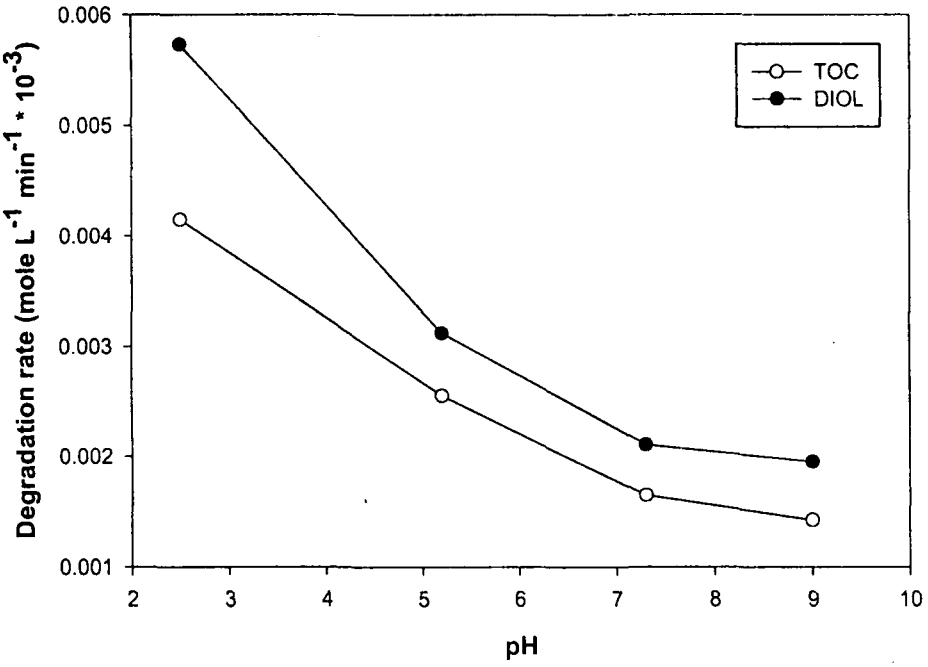


Figure 3.9. Influence of pH on the degradation rate for the mineralization and for the decomposition of N,N-bis(2-hydroxyethyl)dodecanoyl amide (DIOL, **1**). Experimental conditions: 0.2 mM DIOL, V=250 mL, photocatalyst TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (2.5, 5.2, 7.3, and 9.0), irradiation time = 120 min.

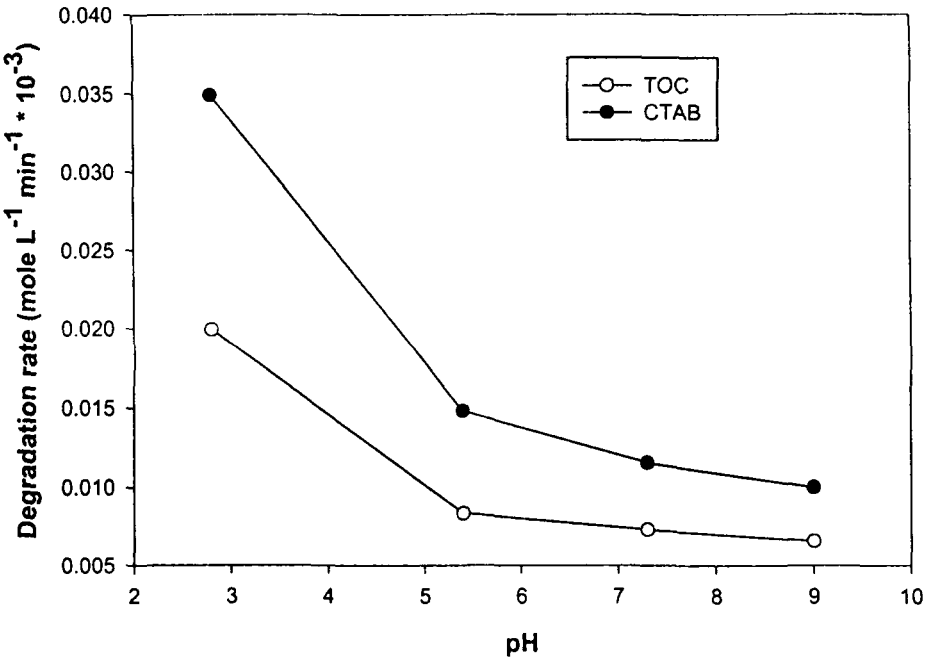


Figure 3.10. Influence of pH on the degradation rate for the mineralization and decomposition of cetyl trimethyl ammonium bromide (CTAB, **2**).
Experimental conditions: 0.2 CTAB, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (2.8, 5.4, 7.3 and 9.0), irradiation time = 90 min.

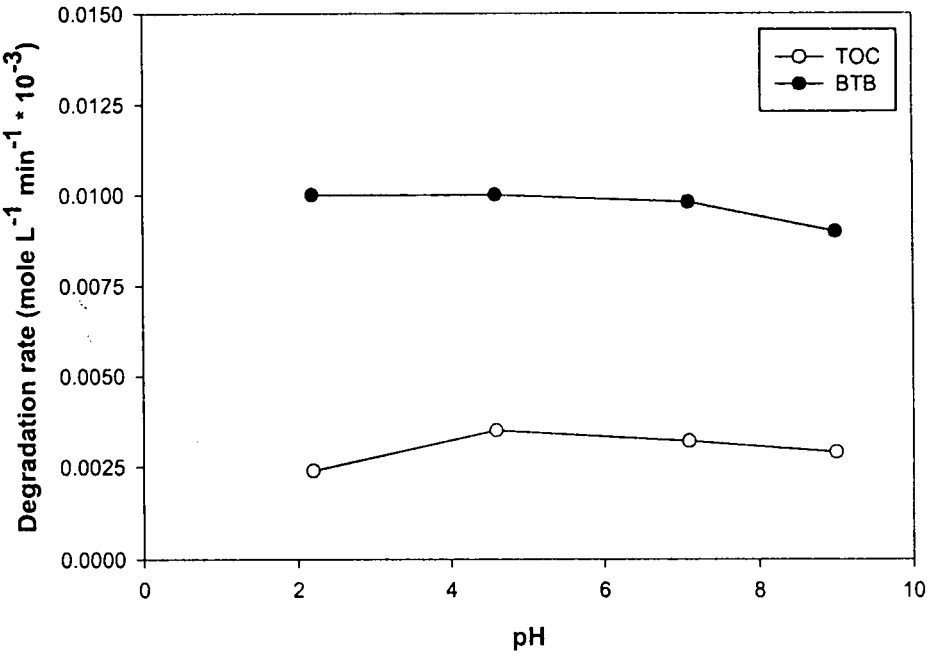


Figure 3.11. Influence of pH on the degradation rate for the mineralization and decomposition of bromothymol blue (BTB, **3**).

Experimental conditions: 0.25 mM bromothymol blue (BTB, V=250 mL, photocatalyst TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (2.2, 4.6, 7.1 and 9.0), irradiation time = 90 min.

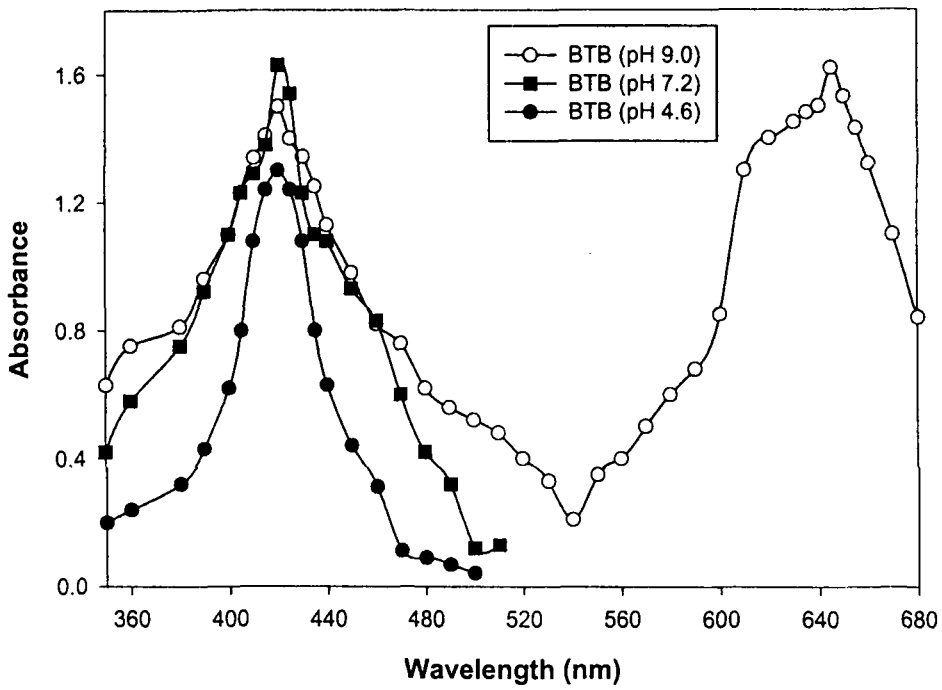


Figure 3.12. Absorption spectra of the dye derivative bromothymol blue (BTB, **3**) at pH values 4.6, 7.1 and 9.0, showing a new peak at wavelength 645nm at pH 9.0.

intensity of the peak appeared at these wavelength were found to decrease as a function of irradiation time. We have followed the decrease in absorption intensity at 420 nm for determining the degradation rate.

The better efficiency for the degradation of both surfactants under acidic pH, may be explained on the basis of protonation and deprotonation of the nitrogen atom present in the molecules, which may lead to favourable structural orientation for the attack of reactive species.

The adsorption of the dye derivative bromothymol blue (**3**) on the surface of the photocatalyst was investigated by stirring their solution in dark for 24 h in a round-bottomed flask containing varying amounts of Degussa P25 at different pH values. Analysis of the sample after centrifugation indicates no observable loss of the dye.

3.4.5 Effect of substrate concentration

The effects of substrate concentration on the degradation of compounds **1-3** was investigated at varying concentrations. Figs. **3.13-3.15** show the degradation rate for the TOC depletion and for the decomposition of compounds **1-3** as a function of substrate concentration employing Degussa P25 as photocatalyst. In case of surfactants **1** and **2** the degradation rate was found to increase with the increase in substrate

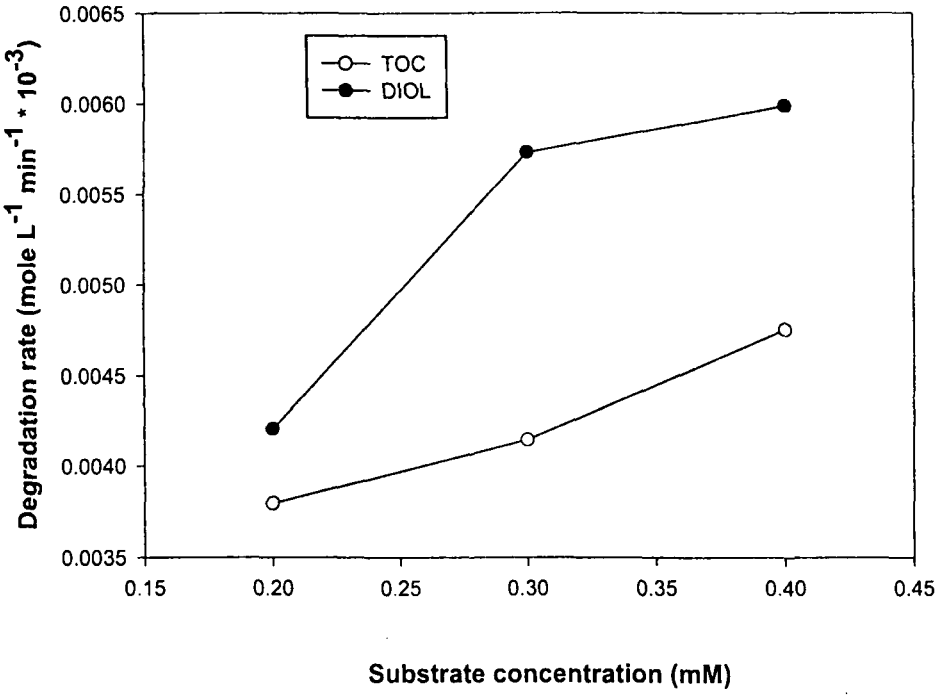


Figure 3.13. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of N,N-bis(2-hydroxyethyl)dodecanoyl amide (DIOL, **1**).

Experimental conditions: substrate concentrations (0.20, 0.30 and 0.40 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 120 min.

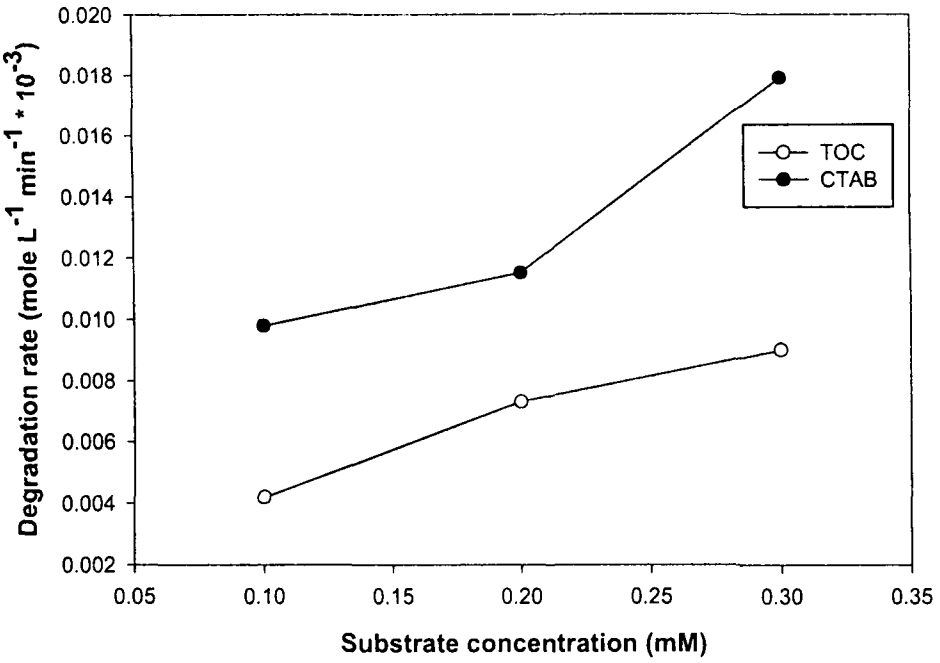


Figure 3.14. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of cetyl trimethyl ammonium bromide (CTAB, **2**).

Experimental conditions: substrate concentrations (0.10, 0.20, and 0.30 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 90 min.

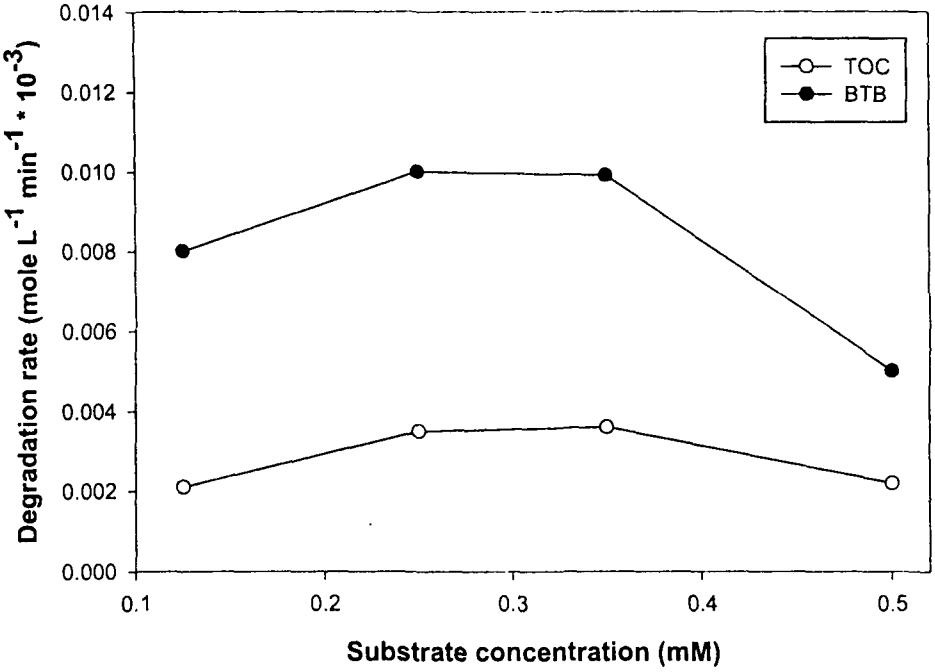


Figure 3.15. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of bromothymol blue (BTB, **3**).
Experimental conditions: substrate concentrations (0.15, 0.25, 0.35 and 0.5 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 90 min.

concentration whereas in case of dye derivative **3**, the rate was found to increase with the increase in substrate concentration from 0.12 mM to 0.35 mM. A further increase in substrate concentration lead to decrease in the degradation rate of the dye. This may be due to the fact that as the initial concentrations of the dye increases, the colour of the irradiating mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. Hence, the generation of relative amount of OH and O_2 on the surface of the catalyst do not increase, as the intensity of light and irradiation time are constant. Conversely, their concentrations will decrease with increase in concentration of the dye as the light photons are largely absorbed and prevented from reaching the catalyst surface by the dye molecules. Consequently, the degradation efficiency of the dye decreases as the dye concentration increases.

3.4.6 Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of **1-3** was investigated employing different catalyst loading of Degussa P25 varying from 0.5 to 3 gL^{-1}. As expected, the degradation rate for the TOC depletion and decomposition of the pollutant was found to

increase with the increase in catalyst concentration as shown in Figs. **3.16-3.18** respectively.

3.4.6 Effect of electron acceptor

The effect of electron acceptor such as hydrogen peroxide, in addition to molecular oxygen on the degradation kinetics of the model compounds **1** and **2** is shown in Figs. **3.19** and **3.20**, respectively. The degradation for the decomposition of the dye derivative **3**, in presence of different electron acceptors is shown in Fig. **3.21**. It has been found that hydrogen peroxide enhance the degradation rate, for the model compounds **1-3**.

The reason for the enhancement of the degradation rate on addition of hydrogen peroxide is already been discussed in chapter 1 and 2.

3.4.7 Intermediate products

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the surfactant **1** in aqueous suspensions of titanium dioxide through GC/MS analysis technique. An aqueous suspension of N,N-bis(2-hydroxyethyl)dodecanoyl amide (**1**, 0.2 mM) was irradiated in the presence of Degussa P25 (1 gL^{-1}) for 120 min with a 125W medium pressure mercury lamp in an immersion well photochemical reactor. The photocatalyst was removed by filteration and the solution was

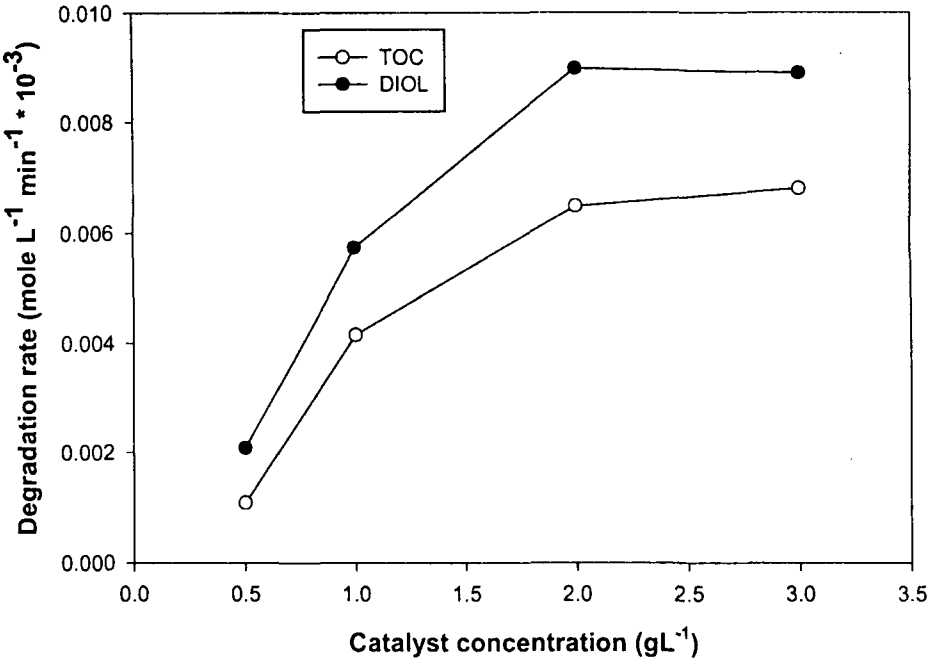


Figure 3.16. Influence of catalyst concentration on the degradation rate for the mineralization and for the decomposition of N,N-bis(2-hydroxyethyl)dodecanoyl amide (DIOL, **1**).

Experimental conditions: 0.2 mM DIOL, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 120 min.

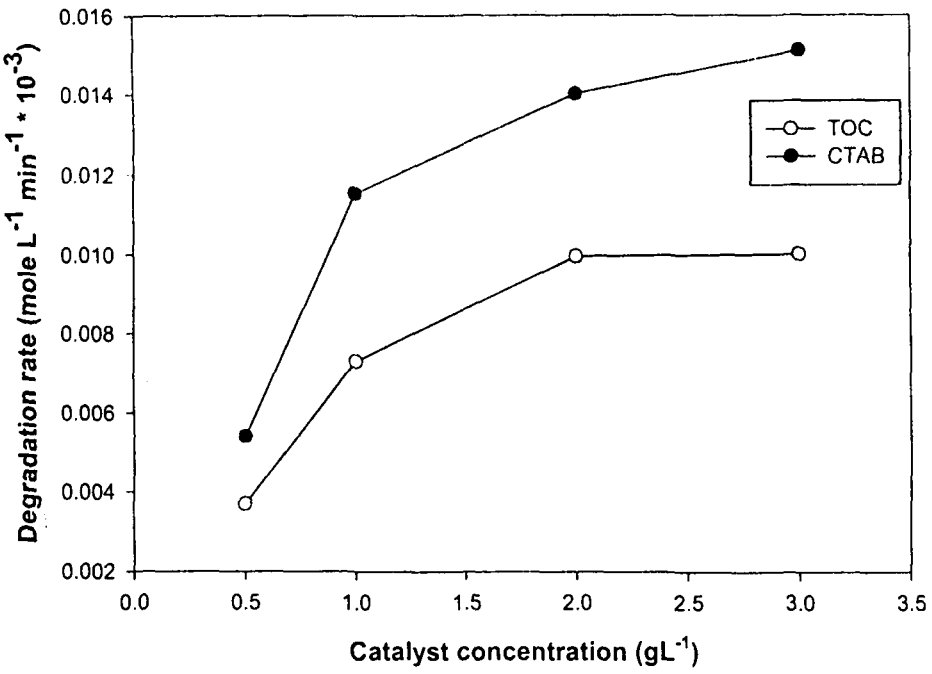


Figure 3.17. Influence of catalyst concentration on the degradation rate for the mineralization and for the decomposition of cetyl trimethyl ammonium bromide (CTAB, **2**).

Experimental conditions: 0.2 mM CTAB, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 90 min.

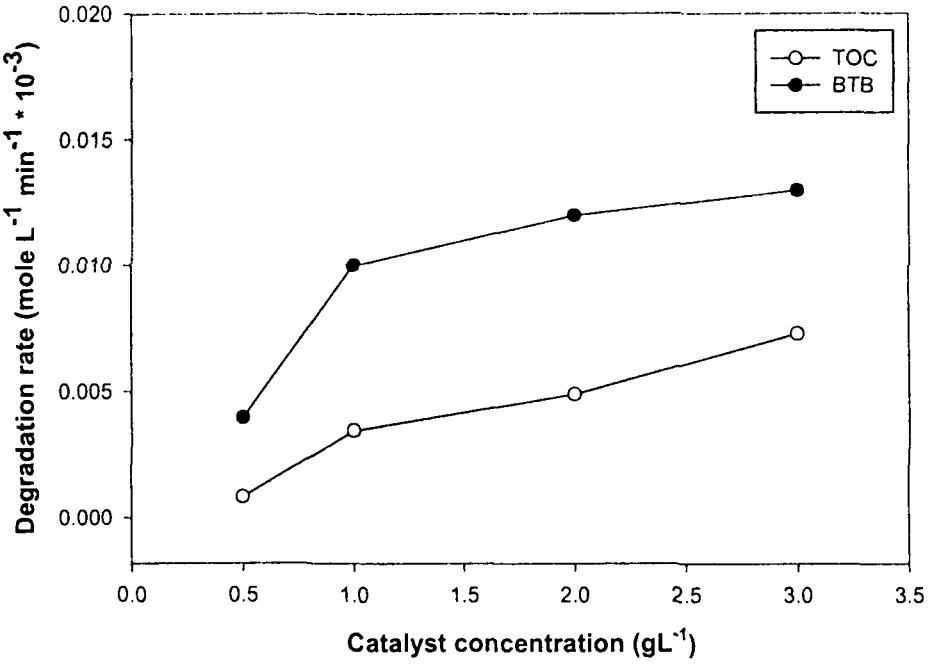


Figure 3.18. Influence of catalyst concentration on the degradation rate for the mineralization and for the decomposition of bromothymol blue (BTB, **3**). Experimental conditions: 0.25 mM BTB, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 90 min.

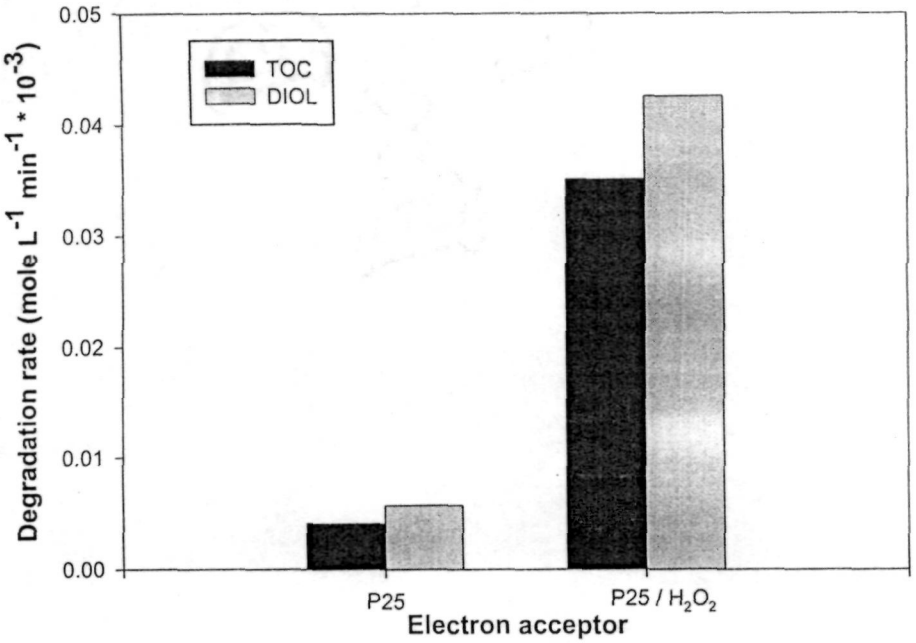


Figure 3.19. Comparison of degradation rate for the mineralization and for the decomposition of N,N-bis(2-hydroxyethyl)dodecanoyl amide (DIOL, **1**) in the presence of hydrogen peroxide.
Experimental conditions: 0.20 mM DIOL, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptor: H_2O_2 (10 mM), irradiation time = 120 min.

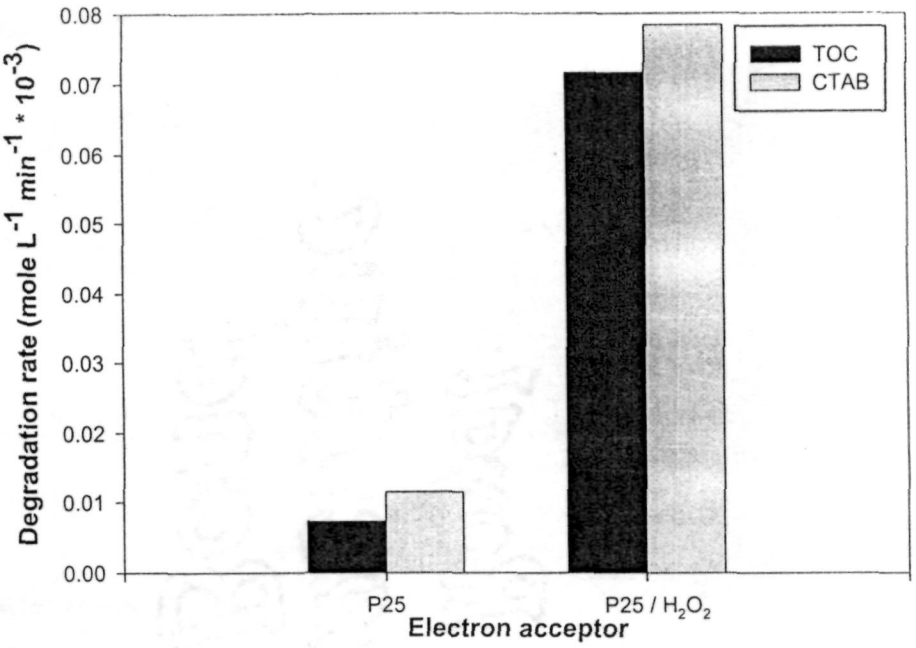


Figure 3.20. Comparison of degradation rate for the mineralization and for the decomposition of cetyl trimethyl ammonium bromide (CTAB, **2**) in the presence of hydrogen peroxide.

Experimental conditions: 0.20 mM CTAB, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptor: H_2O_2 (10 mM), irradiation time = 90 min.

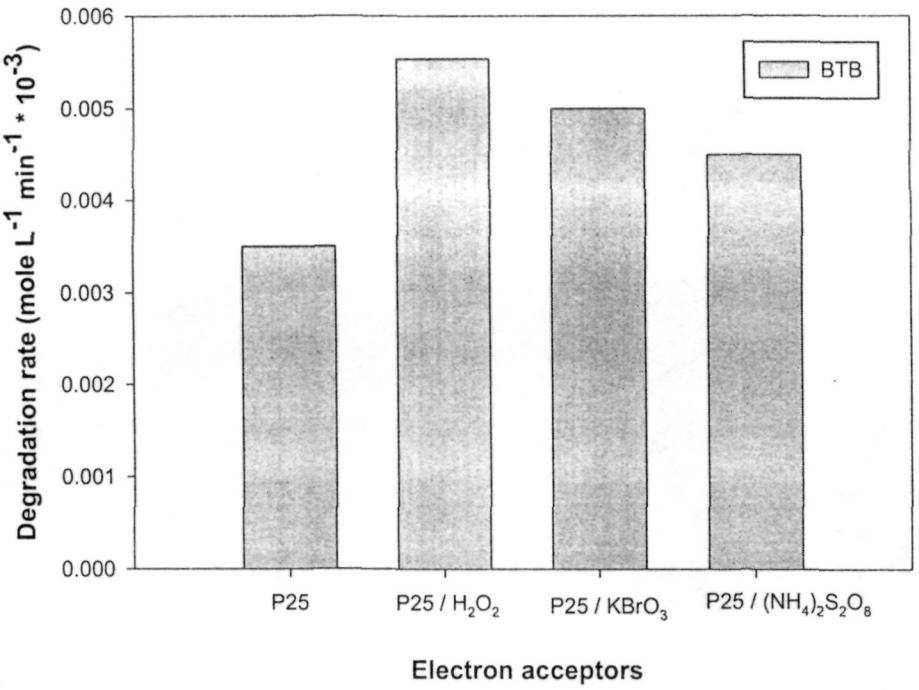
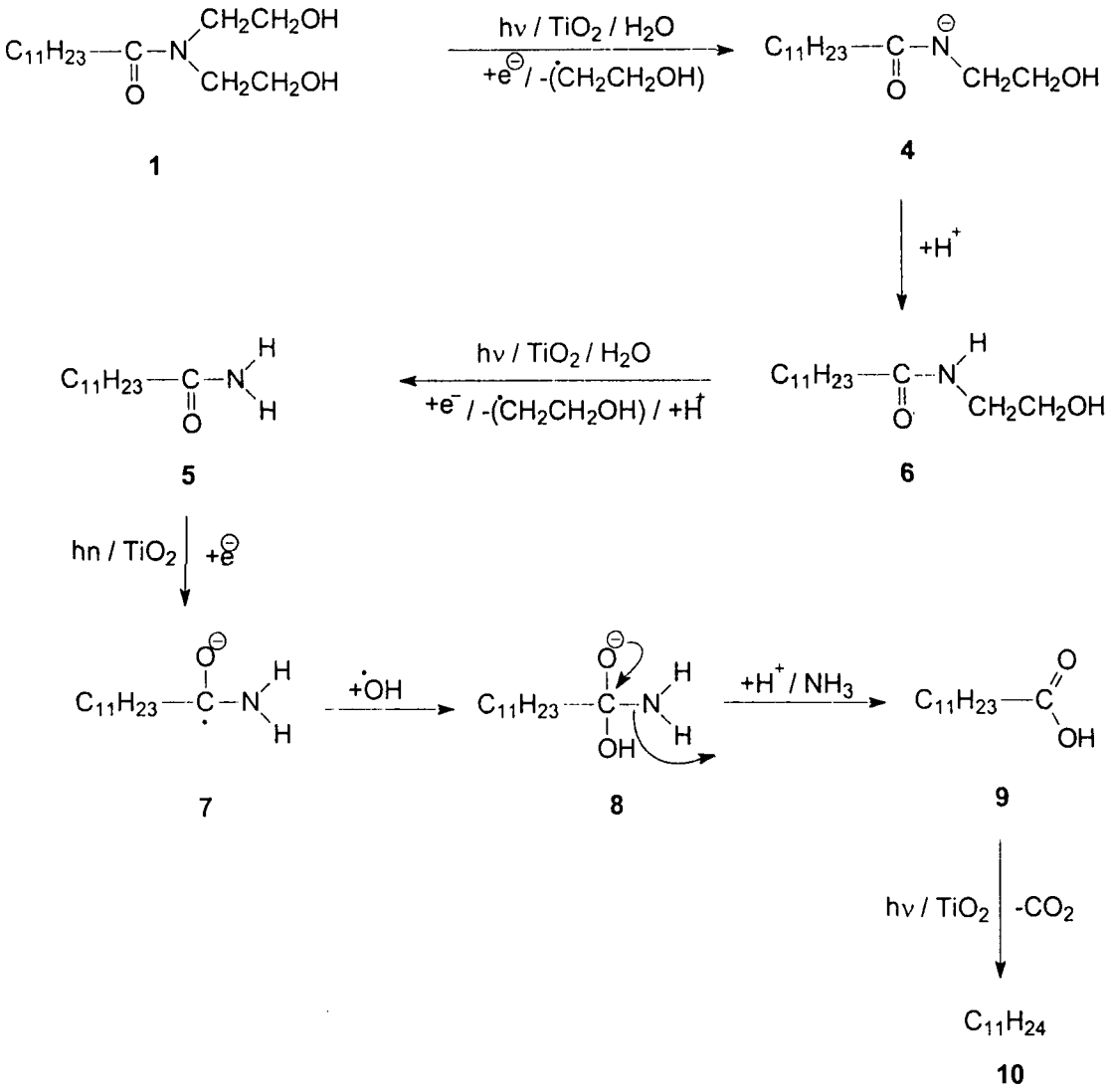


Figure 3.21. Comparison of degradation rate for the decomposition of bromothymol blue (BTB, **3**) in the presence of different electron acceptors.
Experimental conditions: 0.25 mM BTB, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptor: H_2O_2 (10 mM), $KBrO_3$ (3 mM) and $(NH_4)_2S_2O_8$ (3 mM), irradiation time = 90 min.

extracted in chloroform. The removal of the solvent under reduced pressure gave a residual mass, which was analyzed by GC/MS. The GC/MS analysis of the irradiated mixture showed the formation of several products. A probable pathway for the decomposition of the surfactant **1** in aqueous suspension of TiO_2 could be rationalised in term of pathway shown in Scheme **3.1**.


hν / TiO2 / H2O
+e⊖ / -(·CH2CH2OH)
+H+
hν / TiO2 / H2O
+e⁻ / -(·CH2CH2OH) / +H+
hn / TiO2
+e⊖
+·OH
+H+ / NH3
hν / TiO2
-CO2
1
4
5
6
7
8
9
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C11H24

Scheme 3.1

References:

1 M. M. Haque and M. Muneer, *Int. J. Photoenergy* (communicated).

2 M. M. Haque and M. Muneer, *Dyes and Pigm.* (communicated).

3 M. L. Richardson, *J. Soc. Dyers. Colour.*, 99 (**1983**) 198.

4 A. A. Vadya band K. V. Datye, *Colourage,* 29 (**1982**) 3.

5 H. Zollinger, Synthesis, properties and application of organic dyes and pigments In: Colour Chemistry, 1st Ed.;, H.F.Elbel, C.D.Brenzinger, Eds, VCH, Inc.: New york, **1987**.

6 C. E. Searle, Chemical Carcinogenesis, ACS Monograph, American Chemical Society, Washington, DC, 1976.

7 C. T. Helmes, C. C. Sigman, Z. A. Fund, M. K. Thompson, M. K. Voeltz, M. Makie, P. E. Klein and J. B. Lent, *J. Environ. Sci. health A: Chem.,* 19 (**1984**) 97.

8 M. Boeninger, Carcinogenicity and Metabolism of Azo Dyes, Especially Those Derived from Benzidine, DHHS (NIOSH), Publication No. 80-119, July 1980.

9 J. J. Roxan, A.J. Ryan and S. E. Wright, *Food Cosmet. Toxicol.,* 12 (**1967**) 367.

10 K. Vinodgopal and P. V. Kamat. *J. Photochem. Photobiol. A: Chem.*, 83 (**1994**) 141.

11 K. Vinodgopal, I. Bedja, S. Hotechandani and P. V. Kamat, *Langmuir*, 10 (**1994**) 1767.

12 S. Ruan, F. Wu, T. Zhang, W. Gao, B. Xu and M. Zhao, *Mater. Chem. Phys.*, 69 (**2001**) 7.

13 T. Takagishi and N. Katsudu, Int. Conf. Exhib. AACTT., **1999,** 358.

14 K. Kunito, S. Maeda and S. Hongyo, *Okayama-ken kogyo Giyutsu Senta*, 26 (**2000**) 19.

15 G. M. Zamina, N. K. Zaitsev, D. V. Krasnyi, A. L. Karasev and A. V. Vannikov, *High Energy Chem.,* 34 (**2000**) 376.

16 Y. Xu and C. H. Langford, *Langmuir*, 17 (**2001**) 897.

17 T. C-K. Yang, Lin-Shu-yin, W. Guo, T-H Chung and S-F. Wang Tsai, *Adsorpt. Sci. Technol. Proc. Basin. Conf. 2nd National Taipei University of Technology, Taipei, Taiwan, Eds.; D. Do Duong, Singapore,* **2000**, 683.

18 K. Hirano, E. Suzuki, A. Ishikawa, T. Moroi, H. Shiroishi and M. Kaneko, *J. Photochem. Photobiol. A: Chem.,* 136 (**2000**) 157.

19 M. Sökmen and A. Özkan, *J. Photochem. Photobiol. A: Chem.,* 147 (**2002**) 77.

20 C. Hachem, F. Bocquillon, O. Zahara and M. Bouchy, *Dyes and Pigm.*, 49 (**2001**) 117.

21 A. Mills, A. Belghazi, R. H. Davies, D. Worsely and S. Morris, *J. Photochem. Photobiol. A: Chem.*, 79 (**1994**) 131.

22 M. Vautier, C. Gillard and J. M. Hermann, J. Catalysis, 201 (**2001**) 43.

23 I. Arsalan, I. A. Balcioglu and D. Bahnemann, *Dyes and Pigm.*, 47 (**2000**) 207.

24 S. Sakthivel, B. Nappolian, B. Arabindo, M. Palanichamy and V. Murugasen, *Ind. J. Engg. Mat. Sci.*, 7 (**2000**) 87.

25 J. Zhao, V. Wu, K. Wu, K. Oikawa, H. Hidaka and N. Serpone, *Environ. Sci. Technol.*, 32 (**1998**) 2394.

26 M. Muneer, R. Philips and S. Das, *Res. Chem. Intermed.*, 23 (**1997**) 233.

27 M. Saquib and M. Muneer, *Adv. Col. Sci. Technol.*, 5 (**2002**) 71.

28 B. Singhal, G. Patel, J. Vardia and S. C. Ameta, *Poll. Res.* 19 (**2000**) 219.

29 H. Hidaka, H. Kubota, M. Gratzel, E. Palizzetti and N. Serpone, *J. Nouv. Chim.*, 9 (**1985**) 67.

30 H. Hidaka, H. Kubota, M. Gratzel, E. Palizzetti and N. Serpone, *J. Photochem. Photobiol. A: Chem.*, 35 (**1986**) 219.

31 H. Hidaka, S. Yamadam, S. Suenaga, H. Kubota, M. Gratzel, E. Pelizezetti and N. Serpone, *J. Photochem. Photobiol. A: Chem.*, 47 (**1989**) 103.

32 J. Lea and A. Adesina, *J. Photochem. Photobiol. A: Chem.*, 118 (**1998**) 111.

33 E. Pelizzetti, C. Minero, V. Maurino, A. Sclafani, H. Hidaka and N. Serpone, *Environ. Sci. Technol., 23 (**1989**) 1380.*

34 S. Horikoshi, J. Zhao, and H. Hidaka, *J. Jpn. Oil Chem. Soc.* 48 (**1999**) 767.

35 H. Hidaka, K. Nohara, S. Horikoshi, N. Tanaka, S. Watanabe, J. Zhao, and N. Serpone, *J. Jpn. Oil Chem. Soc.* 45 (**1996**) 21.

36 M. Subrahmanyam, K. V. Subba Rao, M. Rajesh Babu and B. Srinivas, *Indian J. Environ. Prot.* 18 (**1997**) 266.

37 Prof. H. Hidaka, Frontier Research Centre for the Global Environment Protection (EPFC), Meisei University, Tokyo, Japan.

38 The photocatalyst Degussa P25 was a gift sample from Degussa-Huls, Frankfurt/Main, Germany.

39 The photocatalyst PC 500 and Hombikat UV100 was a gift sample Dr. D. Bahnemann from the Institut fuer Technische Chemie Universitat Hannover Callinstrasse, Hannover, Germany.

40 The photocatalyst TTP was obtained from Travancore Titanium Products, Kerala, India.

41 The Total Organic Carbon Analyzer was gift equipment from the Alexander von Humboldt-Stiftung, Bonn, Germany.

42 GC/MS analysis was carried out from Sophisticated Instrumentation Center, Indian Institute of Technology, Powai, Mumbai, India.

Chapter 4

PHOTOCATALYSED DEGRADATION OF THREE SELECTED ANTIBIOTICS, NORFLOXACIN, CIPROFLOXACIN AND AMOXICILLIN IN AQUEOUS SUSPENSION OF SEMICONDUCTOR[1,2]

4.1 Abstract

The photocatalysed degradation of three selected antibiotics such as norfloxacin (**1**, 1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline-carboxylic acid), ciprofloxacin (**2**, 1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(piperazine-1-yl)quinoline-3-carboxylic acid hydrochloride) and amoxicillin (**3**, (6R)-6-(a-D-4-hydroxyphenylglycylamino)penicillanic acid trihydrate) have been investigated in aqueous suspension of titanium dioxide under a variety of conditions such as different types of TiO_2, reaction pH, catalyst loading, substrate concentration, and in the presence of different electron acceptors besides molecular oxygen. The degradation of the pollutant was investigated by monitoring the change in substrate concentration employing UV spectroscopic analysis technique and depletion in TOC content as a function of irradiation time. The degradation rate for the decomposition and mineralization of antibiotics was found to be strongly influenced by all the above parameters. The photocatalyst

Degussa P25 was found to be more efficient for the degradation of all the model compounds.

4.2 Introduction

Polluted water pose a serious problem to the environment. Besides water pollutants such as pesticides, dyes and surfactants, pharmaceuticals are an emerging class of aquatic contaminants. Both human and veterinary pharmaceuticals, have been increasingly detected in sewage water, natural water, surface water and ground water.[3-10] The main problem regarding the pharmaceutical as pollutants is that their biological activity leads to adverse effects on aquatic ecosystems.[3-5,8,11,12] They also create adversely effects on soil organism. They enter into the aquatic environment mainly through treated and untreated sewage and human excretion into wastewater. They also enters into the aquatic system via dispersion of manure onto agricultural soils or via urban runoff from farms, where animals are even more overmedicated than humans. The waste pharmaceutical and its derivatives also enter the environment through effluents from pharmaceutical industries.

Among the antibiotic drugs, fluoroquinolone group is probably the most important class of synthetic antibiotics in human and veterinary medicines worldwide[13]. Norfloxacin and Ciprofloxacin are the major

human-use fluoroquinolone. Fluoroquinolone are excreted largely unchanged and about less than 25% are metabolized in the body.[14] Thus most of the fluoroquinolone are pass out through human and animal excretion as such and enters into the water system. Amoxicillin is another class of antibiotic, which comes under penicillin group and is used against broad spectrum of bactericidal activity against gram-positive and gram-negative microorganism. Most of the pharmaceutical compounds have polar structure, so they are not significantly adsorbed in the subsoil but they may leach into the groundwater aquifers from the contaminated surface water. Therefore many drugs are detected in sewage effluents, groundwater, surface and drinking water all over the world. Norfloxacin[9,12] and Ciprofloxacin[9,10,12] have been detected in waste water streams.

Photodegradation by direct excitation of few drugs have been reported earlier.[15-20] These studies have indicated that diclofenac undergo rapid photodegradation, whereas ketoprofen and naproxen undergo slow photodegradation. In contrast ibuprofen is most likely not degraded by direct photolysis in aquatic systems.

To the best of our knowledge no efforts have been made to study the semiconductor mediated photosensitized degradation of above mentioned drugs. Therefore we have made an attempt to study the detail

degradation kinetics of three selected antibiotics such as norfloxacin (**1**), ciprofloxacin (**2**) and amoxicillin (**3**) (Chart **4.1**) in aqueous suspensions of TiO_2 under a variety of conditions.

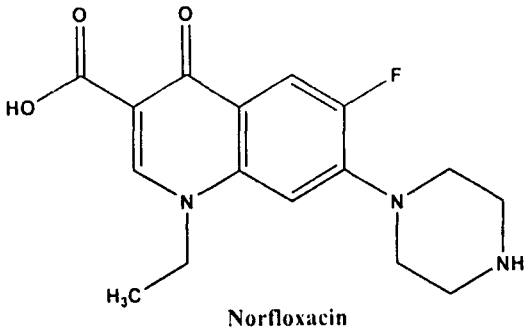
4.3 Experimental

4.3.1 Reagent and chemicals

The antibiotic sample norfloxacin (**1**), was obtained from Cipla, India whereas ciprofloxacin (**2**) and amoxicillin (**3**) was a gift samples from Prof. J. Seetharamappa,[21] who obtained these samples from CDH, New Delhi. These compounds were used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst, titanium dioxide samples such as Degussa P25,[22] Hombikat UV100 (Sachtleben chemie GmbH),[23] PC500 (Milenium inorganic chemicals)[23] and TTP (Travancore titanium products, India)[24] were used for the degradation studies. The other chemical used in this study such as NaOH, HNO_3, $(NH_4)_2S_2O_8$, H_2O_2 and $KBrO_3$ were obtained from Merck.

4.3.2 Procedure

Stock solutions of antibiotics containing the desired concentration (0.25mM) were prepared in double distilled water for irradiation experiments. Due to low solubility of compounds **1** and **3** in water, aqueous

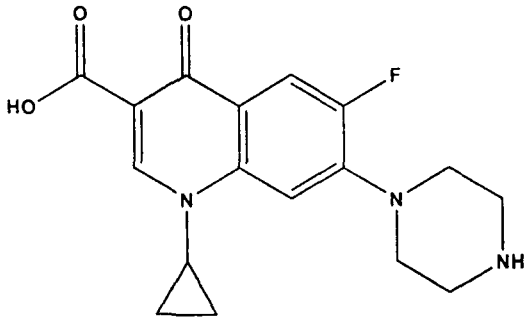


Norfloxacin

1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline-carboxylic acid

$C_{16}H_{18}FN_3O_3$

1

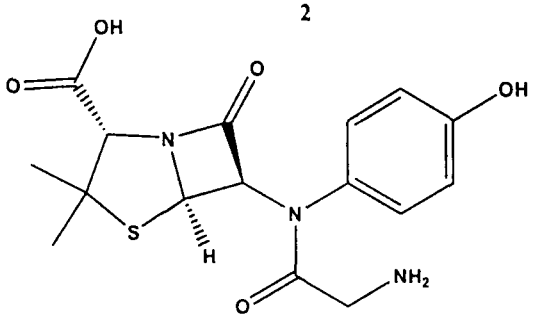


Ciprofloxacin

1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(piperazine-1-yl)quinoline-3-carboxylic acid hydrochloride

$C_{17}H_{18}FN_3O_3 \cdot HCl$

2



Amoxicillin

(6R)-6-(a-D-4-hydroxyphenylglycylamino)penicillanic acid trihydrate

$C_{16}H_{19}N_3O_5S \cdot 3H_2O$

3

Chart 1.1 Chemical structure, common name, chemical name and chemical formula.

solution of norfloxacin (**1**, 0.25mM) was prepared in 2 liters double distilled water by adding 2 ml of 0.5 M aqueous NaOH solution for irradiation experiments. Whereas for amoxicillin (**3**), 0.25mM solution was prepared in 2 liters double distilled water by adding 1 ml of 0.5M aqueous NaOH solution. In case of ciprofloxacin (**2**) the aqueous solution of desired concentration was prepared in double distilled water.

An immersion well photochemical reactor made of Pyrex glass having water circulating jacket equipped with a magnetic stirring bar, and an opening for supply of molecular oxygen was used for the irradiation experiments. The required amount of photocatalyst was added and the solution was stirred and bubbled with molecular oxygen for at least 15 minutes in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (Philips). IR-radiations were eliminated by a water-circulating jacket. Samples (10 mL) were collected before and at regular intervals during irradiation and analyzed after centrifugation.

4.3.2 Analysis

The photodegradation of norfloxacin (**1**), ciprofloxacin (**2**) and amoxicillin (**3**) were measured using UV spectroscopic analysis technique (Shimadzu UV-Vis 1601). The degradation was followed by measuring the decrease in absorption intensity at their λ_{max} as a function of irradiation time. The mineralization of norfloxacin (**1**) was monitored by measuring the depletion in TOC as function of irradiation time using Shimadzu 5000 A TOC Analyzer.[25]

4.4 Results and Discussion

4.4.1 Irradiation of an aqueous solution of norfloxacin (1), Ciprofloxacin (2) and amoxicillin (3) in the presence of TiO_2

Irradiation of an aqueous solution of compounds **1-3**, in the presence of photocatalyst (Degussa P25, 1 gL^{-1}) with a Pyrex filtered out put of a 125 W medium pressure mercury lamp under oxygen lead to decrease in the absorption intensity of the compounds as a function of time. Fig. **4.1** shows the change in absorption intensity and depletion in TOC content as function of time on irradiation of an aqueous suspension of norfloxacin (**1**) in the presence and absence of the photocatalyst. Figs. **4.2** and **4.3** show the change in absorption intensity as function of time on

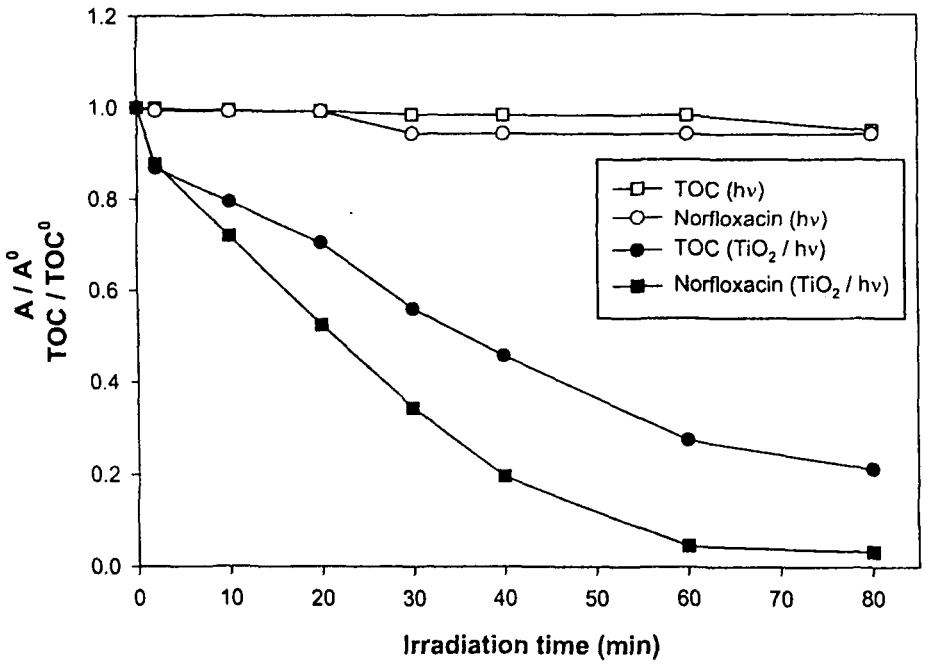


Figure 4.1. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of norfloxacin (1) in the presence and absence of photocatalyst.

Experimental conditions: 0.25 mM norfloxacin, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 284 nm, cont. O_2 purging and stirring, irradiation time = 80 min.

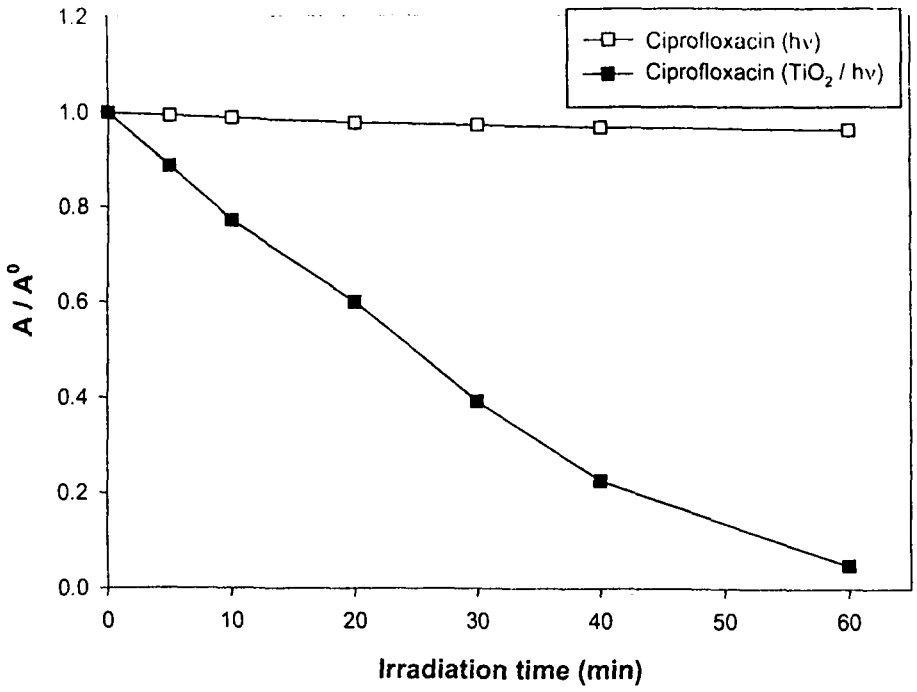


Figure 4.2. Change in absorption intensity at 201 nm as a function of irradiation time for an aqueous solution of ciprofloxacin (**2**) in the presence and absence of photocatalyst.

Experimental conditions: 0.20 mM ciprofloxacin, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 60 min.

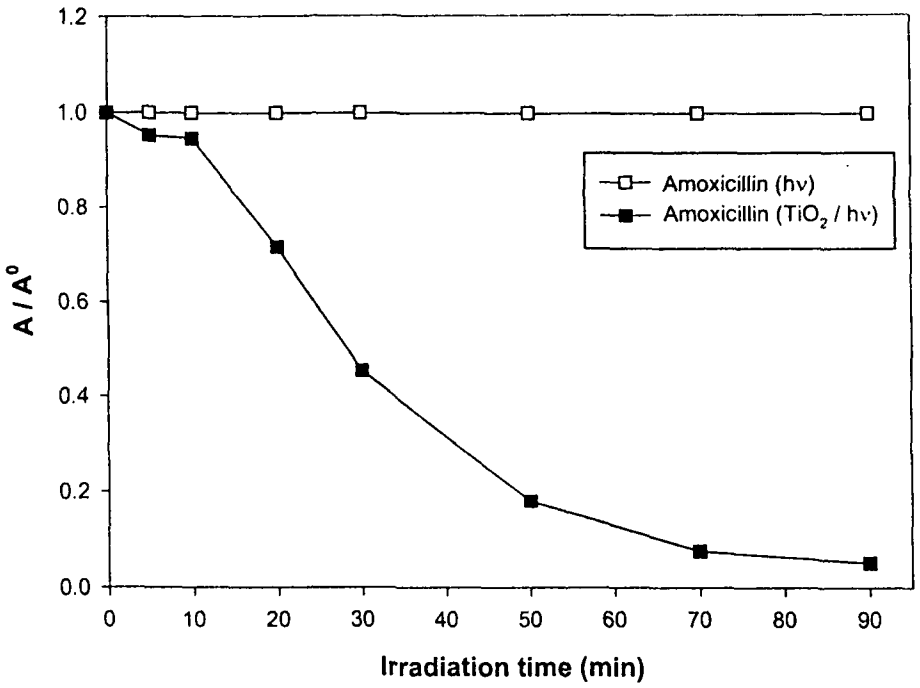


Figure 4.3. Change in absorption intensity at 228.5 nm as a function of irradiation time for an aqueous solution of amoxicillin (**3**) in the presence and absence of photocatalyst.

Experimental conditions: 0.20 mM amoxicillin, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 90 min.

irradiation of an aqueous suspension of ciprofloxacin (**2**) and amoxicillin (**3**), respectively, in the presence and absence of the photocatalyst. It could be seen from the figure that the loss of compound was negligible when the irradiation was carried out in absence of photocatalyst.

The decomposition (change in absorption intensity Vs irradiation time) and mineralization (depletion in TOC content Vs irradiation time) curves of all the compounds under investigation could be fitted reasonably well by an exponential decay curve suggest first order degradation kinetics i.e. linear regression plot of natural logarithm of absorption intensity and TOC Vs irradiation time. For each experiments, the rate constant was calculated from the plot of natural logarithm of TOC and the substrate concentration. The degradation rate for the mineralization and decomposition of the compounds under investigation was calculated using formula given below,

$$\frac{-d[TOC]}{dt} = kc^n \qquad [1]$$

$$\frac{-d[A]}{dt} = kc^n \qquad [2]$$

TOC = Total Organic Carbon, A = absorbance, k = rate constant, c = concentration of the pollutant, n = order of reaction.

The degradation rate for the mineralization and decomposition was calculated in terms of mole L^{-1} min^{-1}.

Control experiments were carried in all cases employing un-irradiated blank solutions. The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

4.4.2 Comparison of the photocatalytic degradability of norfloxacin (1), Ciprofloxacin (2) and amoxicillin (3)

Comparison of decomposition (change in absorption intensity Vs irradiation time) of antibiotics **1-3** (0.2 mM) on irradiation of an aqueous suspension with a 125 W medium pressure mercury lamp in the presence of TiO_2 (Degussa P25, $1gL^{-1}$) for 30 min is shown in Fig. **4.4**. The photodegradability of the three antibiotics can then be ranked in the following order : Norfloxacin > Ciprofloxacin > Amoxicillin.

4.4.3 Comparison of different photocatalysts

We have tested the photocatalytic activity of three different commercially available TiO_2 powders (namely Degussa P25, Hombikat UV100, PC500) on the degradation kinetics of norfloxacin (**1**), ciprofloxacin (**2**) and amoxicillin (**3**). The degradation rate obtained for the TOC depletion and decomposition of compound **1**, in the presence of different

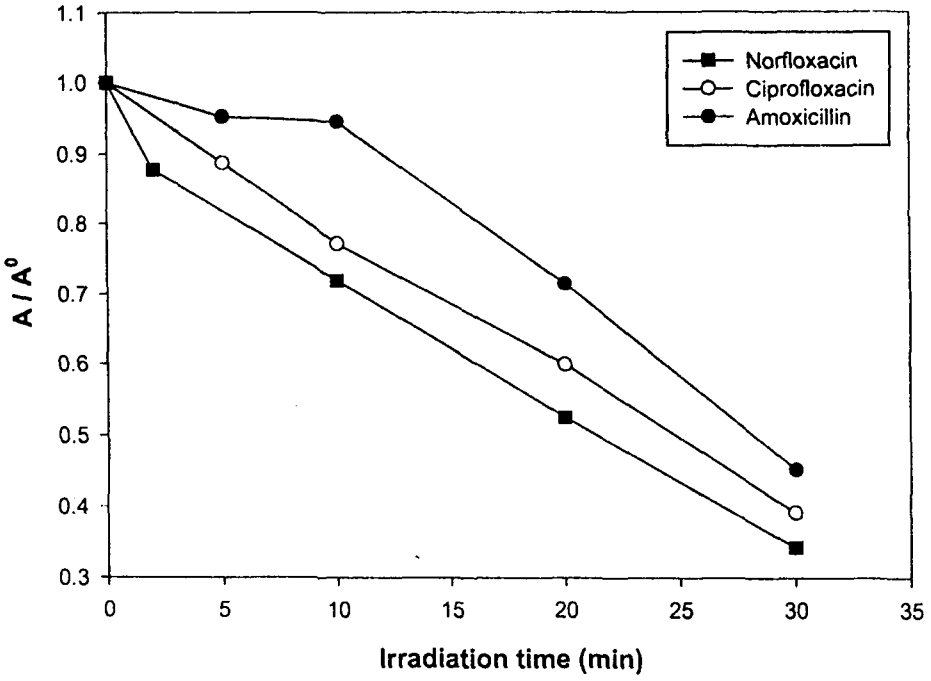


Figure 4.4. Comparison of decomposition (change in absorption intensity Vs irradiation time) of norfloxacin (**1**), ciprofloxacin (**2**) and amoxicillin (**3**). Experimental conditions: antibiotics concentration (**1-3**) 0.2 mM, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), light source 125 W medium pressure Hg lamp, immersion well photoreactor, cont. O_2 purging and stirring, irradiation time = 30 min.

types of TiO_2 powders is shown in Fig. **4.5**. The degradation rate for the decomposition of compounds **2** and **3** as a function of type of photocatalyst is shown in Figs. **4.6** and **4.7**, respectively. The photocatalyst, Degussa P25 has found to be better than other TiO_2 powder for decomposition and mineralization of the compounds under investigation. This photocatalyst has been found to be more efficient for the degradation of majority of organic compounds studied in this thesis and earlier studied systems.[26-29]

The reason for better photocatalytic activity of Degussa P25 have already been discussed in Chapter 1 and 2.

Therefore, in all following experiments the photocatalyst Degussa P25 was used for the degradation of three different antibiotic derivatives under varying conditions.

4.4.4 pH Effect

The influence of pH on the degradation kinetics of norfloxacin (**1**), ciprofloxacin (**2**) and amoxicillin (**3**) in aqueous suspensions of Degussa P25 was studied at different pH values. Fig. **4.8** shows the degradation rate Vs pH for the TOC depletion and decomposition of antibiotic (**1**). The degradation rate for the decomposition of antibiotics **2** and **3** as function of pH are shown in Figs. **4.9** and **4.10**, respectively.

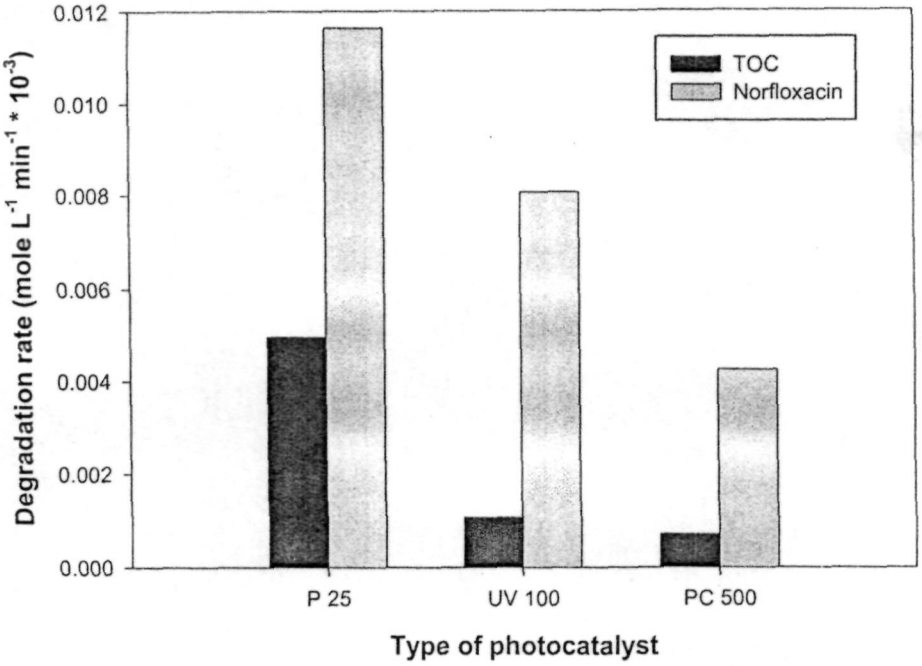


Figure 4.5. Comparison of degradation rate for the mineralization (TOC depletion Vs irradiation time) and decomposition (change in absorption intensity Vs irradiation time) of norfloxacin (**1**) in the presence of different photocatalysts.

Experimental conditions: 0.25 mM norfloxacin, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), irradiation time = 80 min.

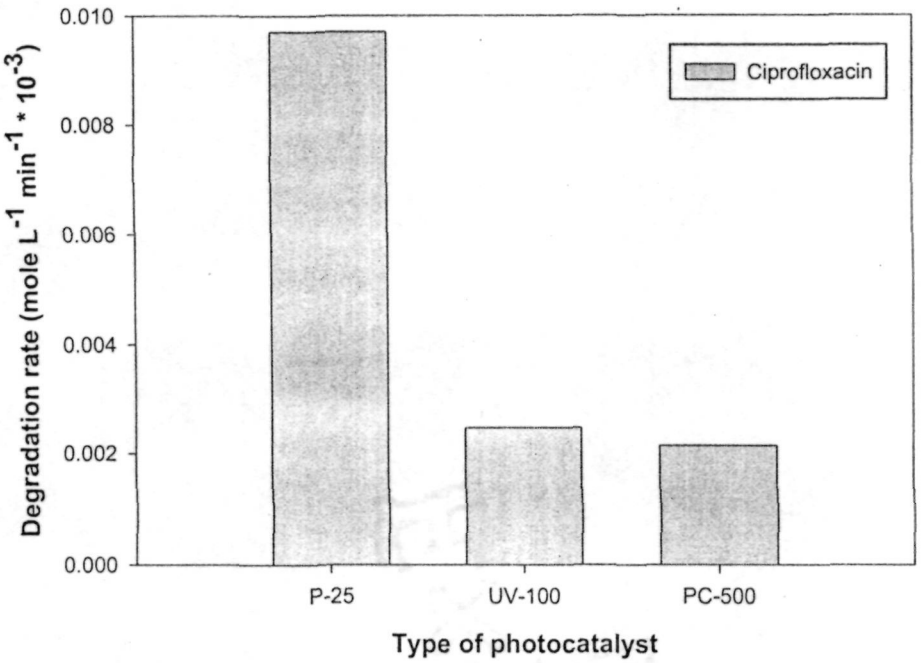


Figure 4.6. Comparison of degradation rate for the decomposition (change in absorption intensity Vs irradiation time) of ciprofloxacin (**2**) in the presence of different photocatalysts.

Experimental conditions: 0.20 mM ciprofloxacin, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), irradiation time = 60 min.

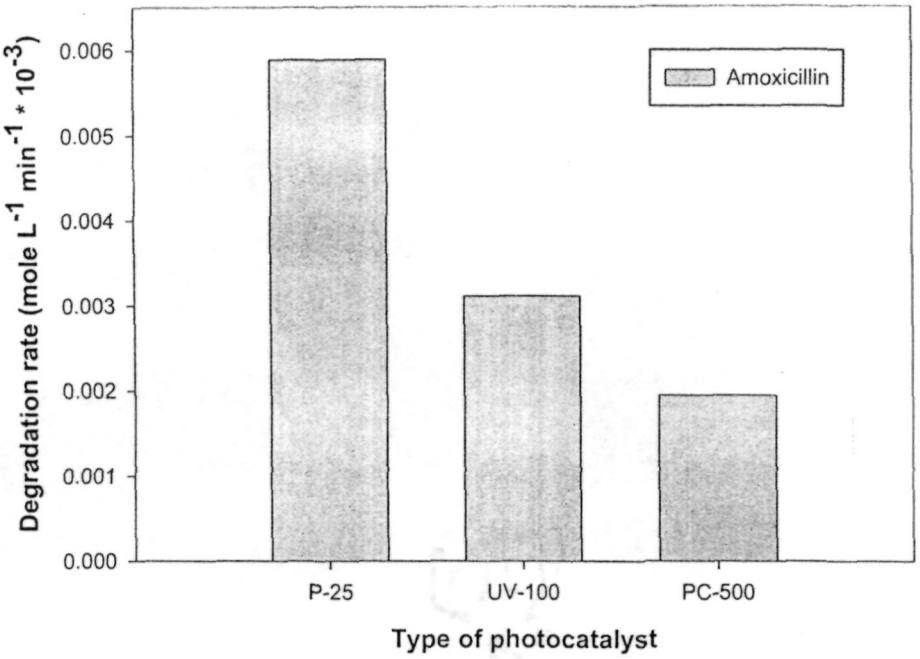


Figure 4.7. Comparison of degradation rate for the decomposition (change in absorption intensity Vs irradiation time) of amoxicillin (**3**) in presence of different photocatalysts.

Experimental conditions: 0.20 mM amoxicillin, V=250 mL, photocatalysts: TiO_2 Degussa P25 (1 gL^{-1}), Sachtleben Hombikat UV100 (1 gL^{-1}), PC500 (1 gL^{-1}), irradiation time = 90 min.

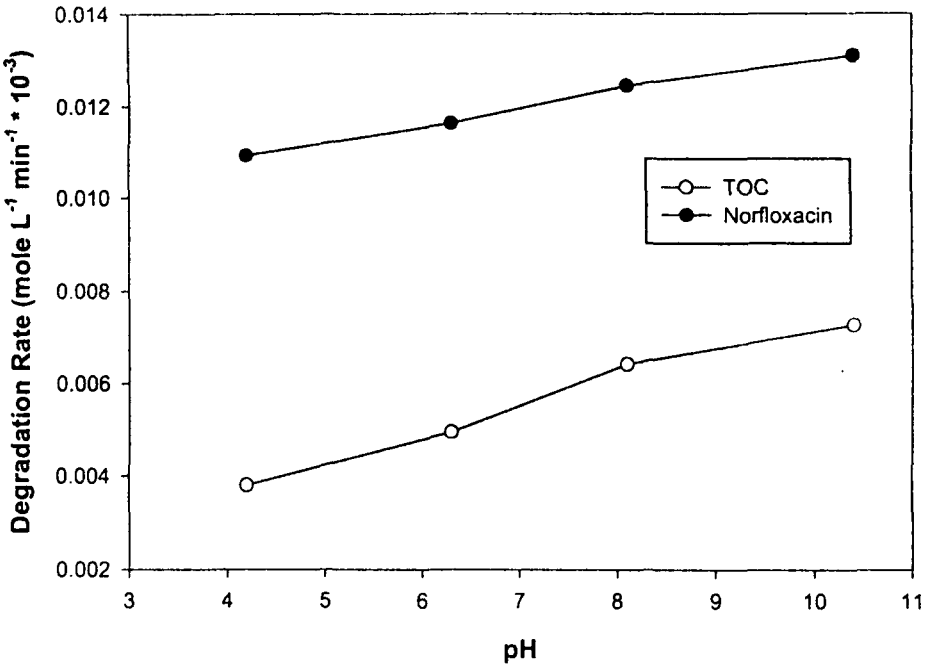


Figure 4.8. Influence of pH on the degradation rate for the mineralization and for the decomposition of norfloxacin (**1**).

Experimental conditions: 0.25 mM norfloxacin, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (4.2, 6.3, 8.1 and 10.4, irradiation time = 80 min.

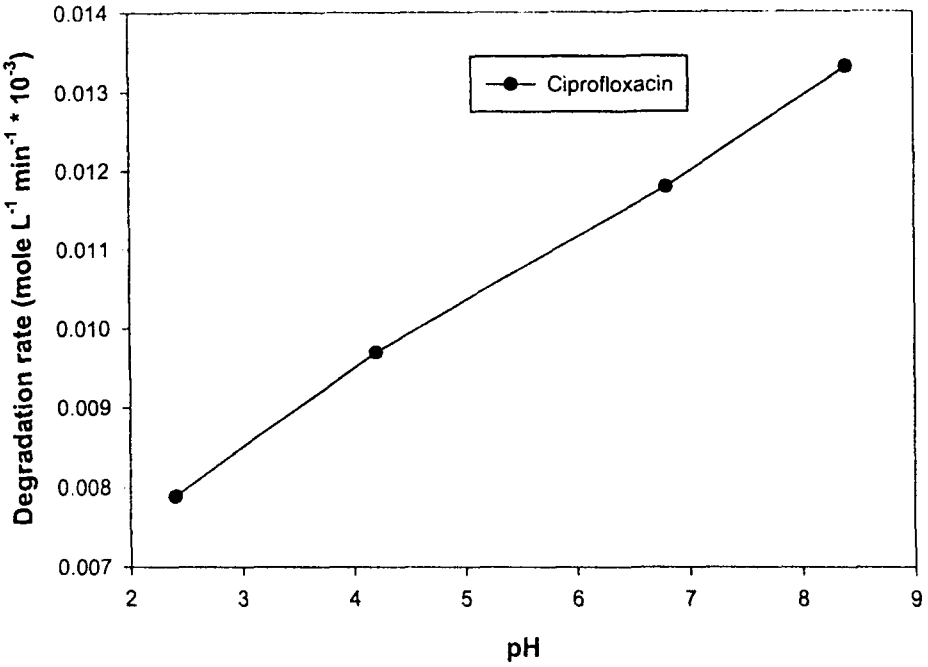


Figure 4.9. Influence of pH on the degradation rate for the decomposition of ciprofloxacin (**2**).
Experimental conditions: 0.20 mM ciprofloxacin, V=250 mL, photocatalyst:TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (2.4, 4.2, 6.8 and 8.4), irradiation time = 60 min.

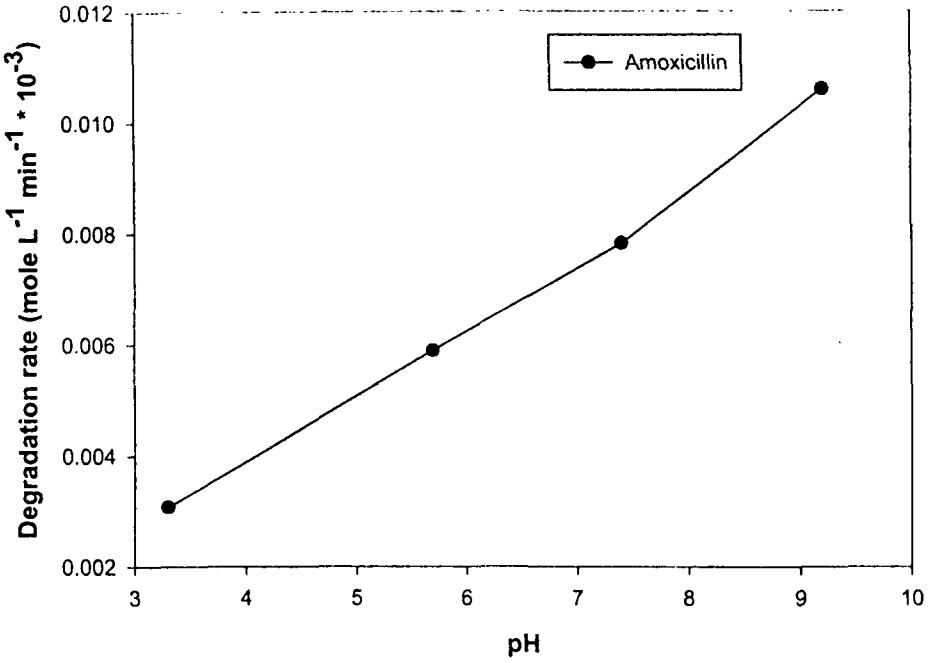


Figure 4.10. Influence of pH on the degradation rate for the decomposition of amoxicillin (**3**).

Experimental conditions: 0.20 mM amoxicillin, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (3.3, 5.7, 7.4 and 9.2), irradiation time = 90 min.

The reaction pH has been found to play an important role and the degradation of all the compounds under investigation was found to increase with the increase in pH in the pH range studied. Interestingly the degradation rate for the decomposition of compounds **2** and **3** was found to increase markedly with the increase in pH of the reaction and the highest efficiency was observed at 8.4 and 10.2, respectively within the pH range studied.

The better efficiency for the degradation of all the compounds (**1-3**) in alkaline pH could be attributed on the basis of efficient generation of hydroxyl radicals by TiO_2 with increasing concentration of OH^-.

4.4.5 Effect of substrate concentration

The influence of substrate concentration on the degradation of compounds **1-3** was investigated at different concentrations varying from 0.1 to 0.50 mM. Fig. **4.11** shows the degradation rate for the TOC depletion and decomposition of antibiotic **1** as a function of substrate concentration employing Degussa P25 as photocatalyst. It could be seen from the figure that the degradation rate for the decomposition increases with the increase in substrate concentration. Whereas, its influence on the rate for the mineralization was not pronounced from 0.25 to 0.5 mM and

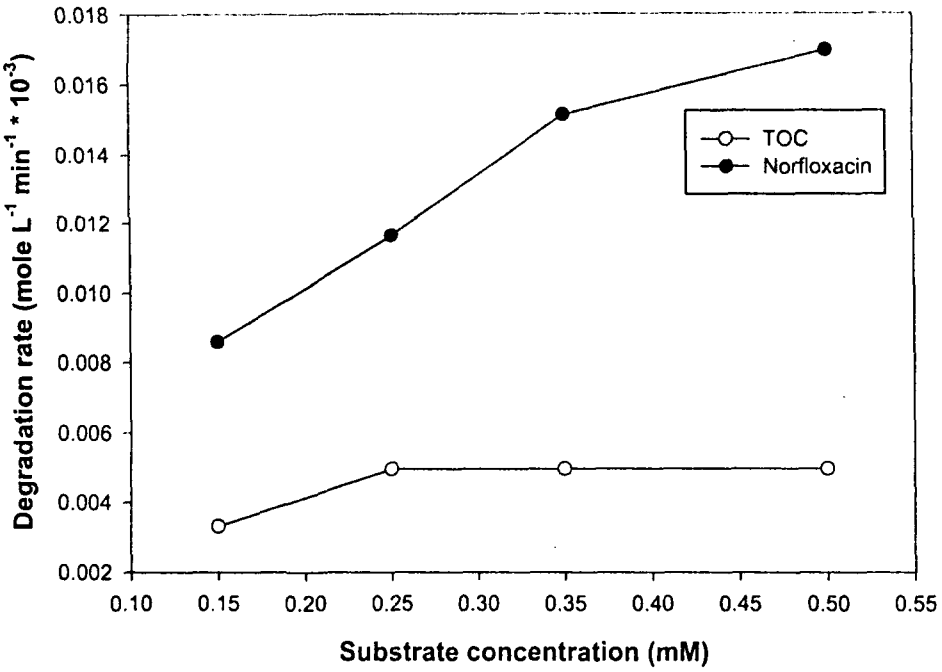


Figure 4.11. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of norfloxacin (1).

Experimental conditions: substrate concentrations (0.15, 0.25, 0.35 and 0.50 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 80 min.

found to be more or less same within the experimental error limits. It increases from 0.15 to 0.25 mM only.

The degradation rate for the decomposition of compounds **2** and **3** was found to increase with the increase in substrate concentration as shown in Figs. **4.12** and **4.13**, respectively.

4.4.6 Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of **1-3** were investigated employing different catalyst loading of Degussa P25 varying from 0.5 to 3 gL^{-1}. As expected, the degradation rate for the TOC depletion and decomposition of the antibiotic **1** was found to increase with the increase in catalyst concentration as shown in Fig. **4.14**.

The degradation rate for the decomposition of antibiotics **2** and **3** was also found to increase with the increase in catalyst concentration as shown in Figs. **4.15** and **4.16**.

4.4.7 Effect of electron acceptor

The effect of electron acceptors such as hydrogen peroxide, potassium bromate and ammonium persulphate in addition to molecular oxygen on the degradation kinetics of the model compounds were investigated as well. It was found that hydrogen peroxide enhances the

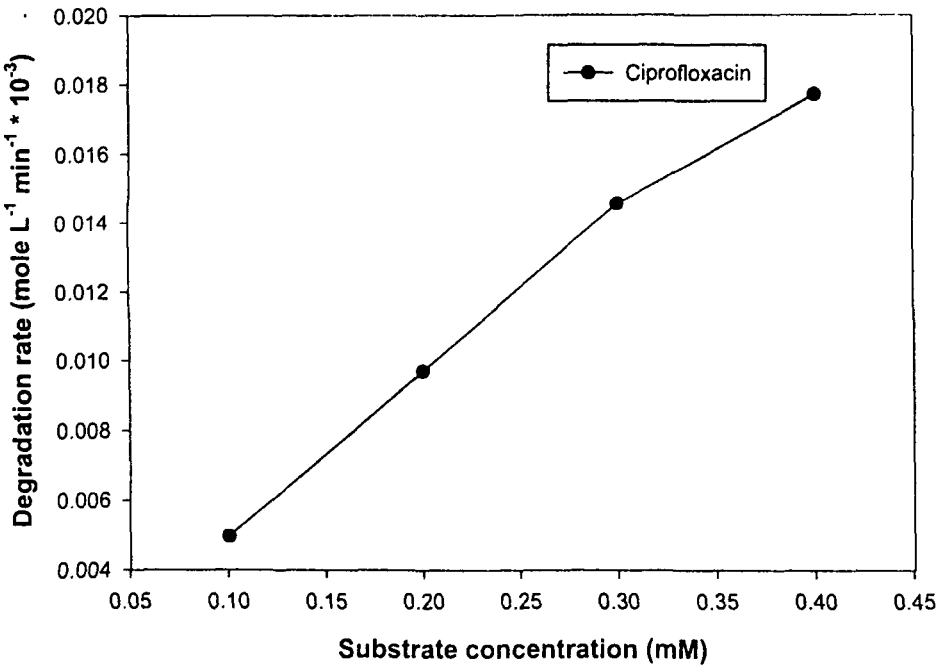


Figure 4.12. Influence of substrate concentration on the degradation rate for the decomposition of ciprofloxacin (**2**).

Experimental conditions: substrate concentrations (0.10, 0.20, 0.30 and 0.40 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1} irradiation time = 60 min.

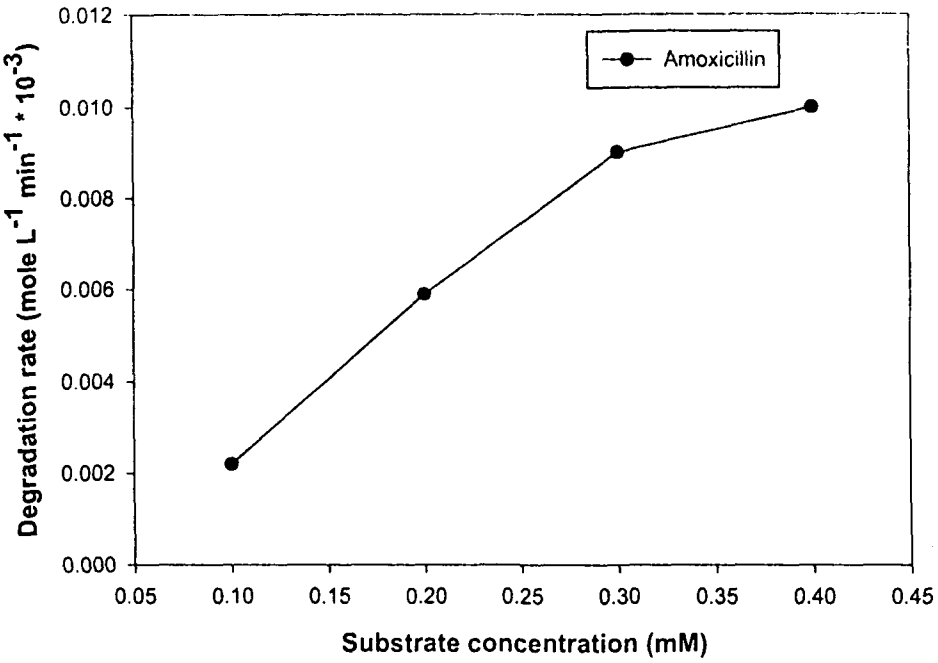


Figure 4.13. Influence of substrate concentration on the degradation rate for the decomposition of amoxicillin (**3**).

Experimental conditions: substrate concentrations (0.10, 0.20, 0.30 and 0.40 mM), V=250 mL, photocatalyst:TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 90 min.

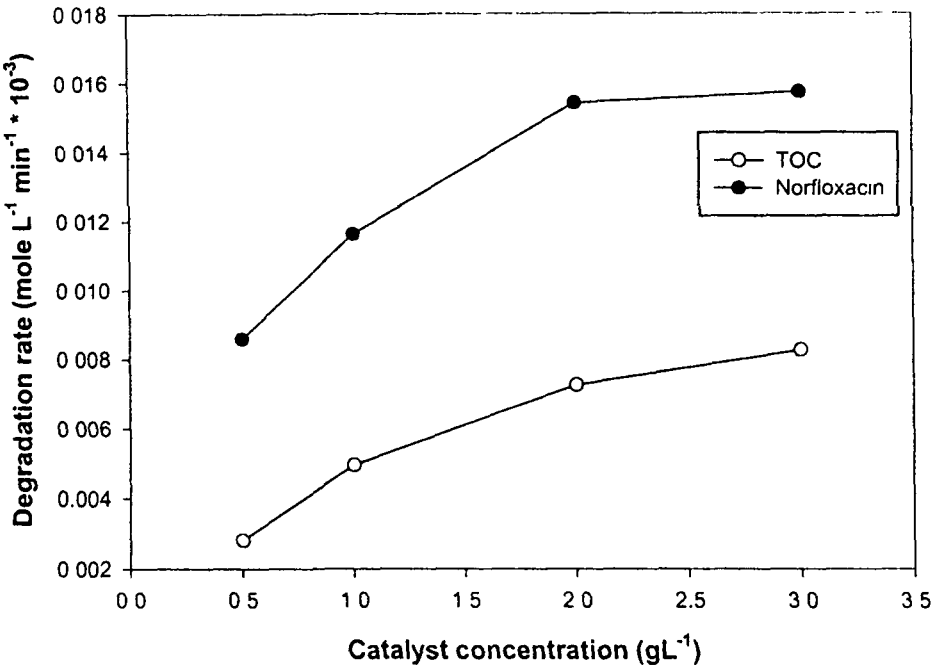


Figure 4.14. Influence of catalyst concentration on the degradation rate for the mineralization and for the decomposition of norfloxacin (**1**).

Experimental conditions: 0.25 mM norfloxacin, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 80 min.

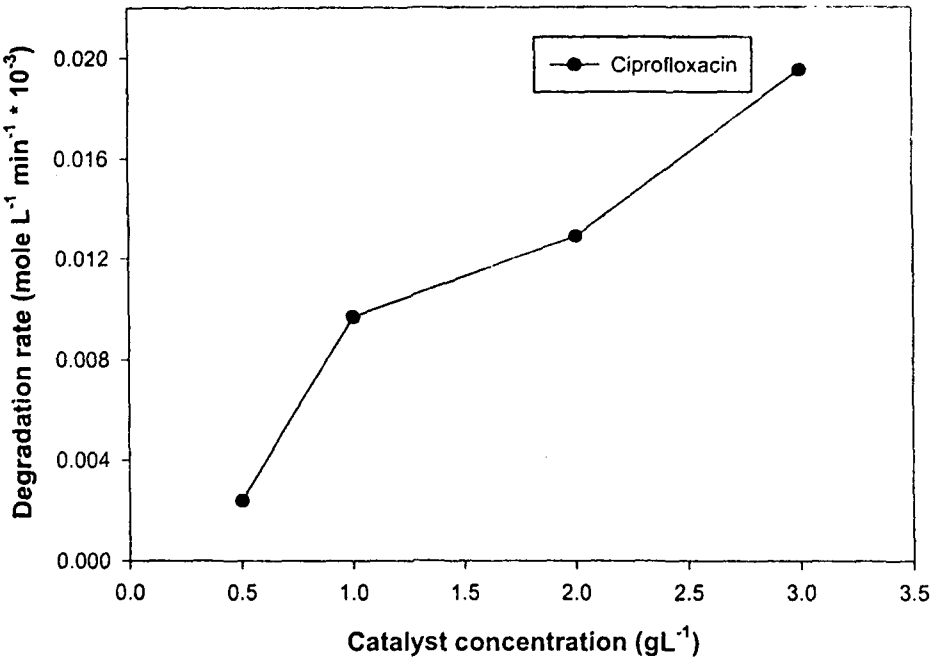


Figure 4.15. Influence of catalyst concentration on the degradation rate for the decomposition of ciprofloxacin (**2**).

Experimental conditions: 0.20 mM ciprofloxacin, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 60 min.

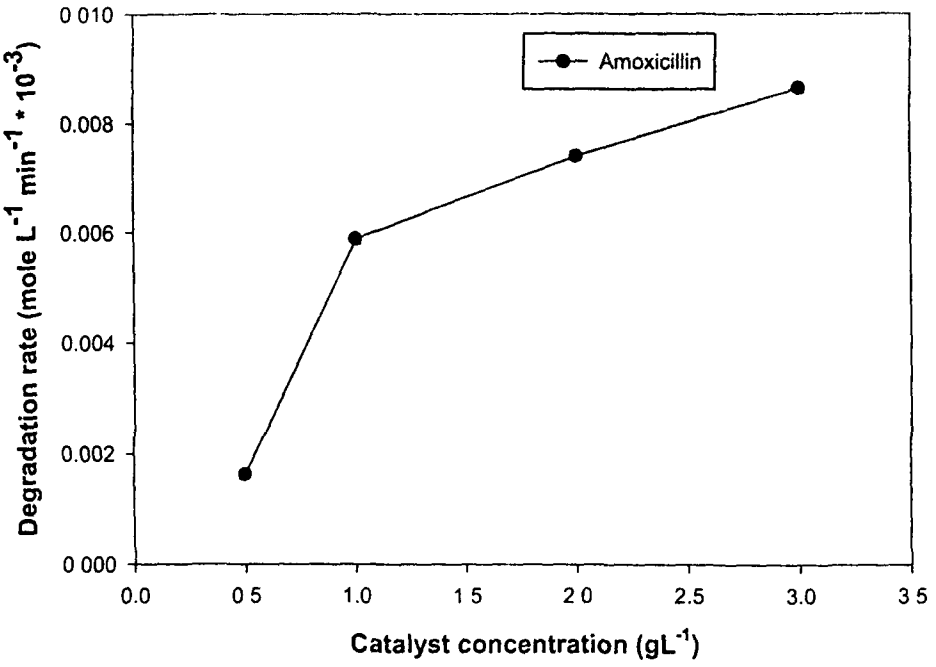


Figure 4.16. *Influence of catalyst concentration on the* degradation rate for the decomposition of amoxicillin (3).

Experimental conditions: 0.20 mM amoxicillin, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 90 min.

degradation rate, for the decomposition and mineralization of antibiotic **1**, as shown in Fig. **4.17**.

In the case of **2**, the electron acceptors such as hydrogen peroxide and potassium bromate enhanced the degradation, whereas the effect of ammonium persulphate was not pronounced as shown in Fig. **4.18**. In contrast, in the case of **3**, all the additives showed beneficial effect as shown in Fig. **4.19**.

It is interesting to note that for the degradation of compound **1**, the addition of hydrogen peroxide markedly enhanced the mineralization rate as compared to the degradation rate.

The reason for the enhancement of the degradation rate in the presence of electron acceptors has already been discussed in Chapter 1 and 2.

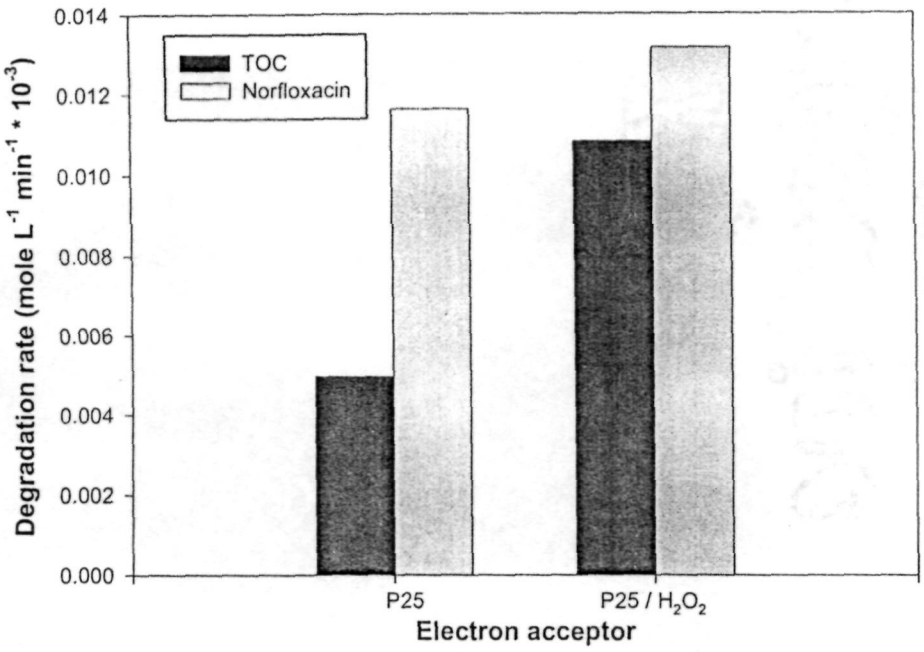


Figure 4.17. Comparison of degradation rate for the mineralization and for the decomposition of norfloxacin (**1**) in the presence of hydrogen peroxide. Experimental conditions: 0.25 mM norfloxacin, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptor: H_2O_2 (10 mM), irradiation time = 80 min.

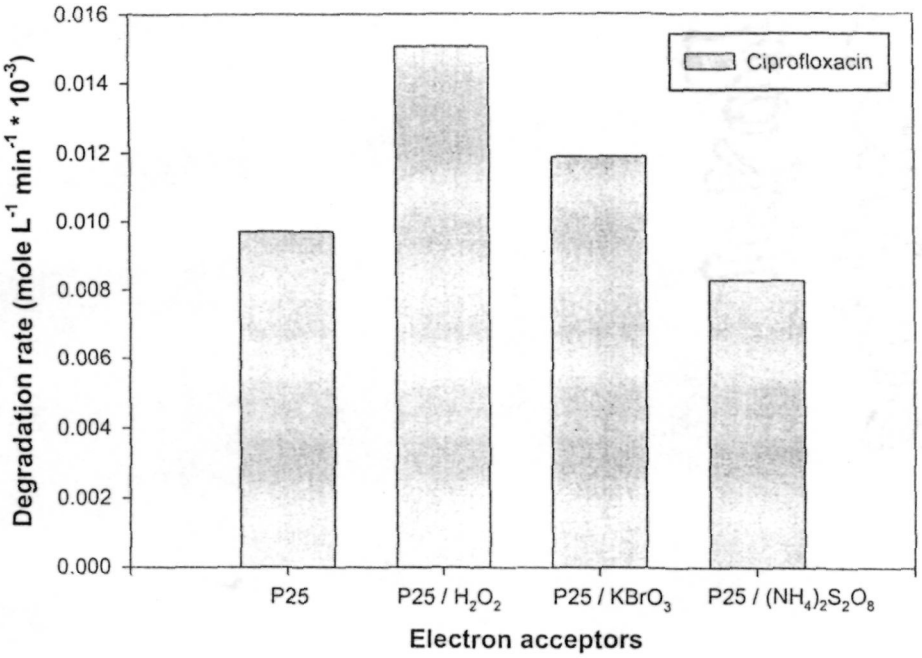


Figure 4.18. Comparison of degradation rate for the decomposition of ciprofloxacin (**2**) in the presence of different electron acceptors.

Experimental conditions: 0.20 mM ciprofloxacin, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 60 min.

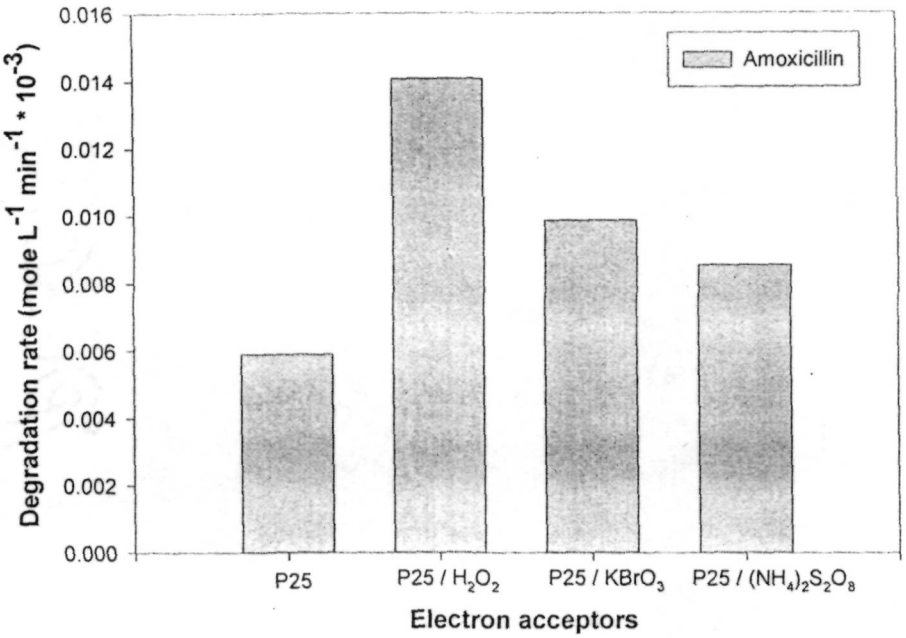


Figure 4.19. Comparison of degradation rate for the decomposition of amoxicillin (**3**) in the presence of different electron acceptors.

Experimental conditions: 0.20 mM amoxicillin, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 90 min.

References:

1 M. M. Haque and M. Muneer, *Sci. Total Environ.*, (under preperation).

2 M. M. Haque and M. Muneer, *Aquat. Sci.*, (under preperation).

3 B. Halleing-Sorensen, S. N. Nielsen, P. F. Lanzky, F. Ingerslev, H. C. Holten Lutzhoft and S. E. Jorgensen, *Chemosphere*, 36 (**1997**) 357.

4 T. A. Ternes, *Water Research*, 32 (**1998**) 3245.

5 C. G. Daughton and T. A. Ternes, *Environ. Health Persp. Suppl.*, 107 (**1999**) 907.

6 M. Stumpf, T. A. Ternes, R. D. Wilkin, R. Silvana Vianna and W. Baumann, *J. Pharmacy and Pharmacology*, 30 (**1999**) 47.

7 E. Zuccato, D. Calamari, M. Natangelo and R. Fanelli, *Lancer*, 355 (**2000**) 1789.

8 O. A. H. Jones, N. Volvlvoulis and J. N. Lester, *Environ. Technol.*, 22 (**2001**) 1383.

9 T. Heberer, *Toxicol. Letters*, 131 (**2002**) 5.

10 D. Calamari, E. Zuccato, S. Castiglioni, R. Bagnati and R. Fanelli, *Environ. Sci. and Technol.*, 37 (**2003**) 1241.

11 R. Hirch, T. Ternes, K. Haberer and K. L. Kratz, *Science of the total Environment*, 222 (**1999**) 109.

12 D. W. Kolpin, E. T. Furlong, M. T. Meyer, E. M. Thurman, S. D. Zaugg, L. B. Barber and H. T. Buxton, *Environ. Sci. and Technol.*, 36 (**2002**) 1202.

13 E. M. Golet, A. C. Alder, A. Hartmann, T. A. Ternes and W. Giger, *Anal. Chem.*, 73 (**2001**) 3632.

14 F. Sörgel and M. Kinzig, *Am. J. Med.*, 94 (**1993**) 56.

15 H. –R. Buser, T. Poiger and M. D. Mueller, *Environ. Sci. Technol.*, 32 (**1998**) 3449.

16 H. –R. Buser, T. Poiger and M. D. Mueller, *Environ. Sci. Technol.*, 33 (**1999**) 2529.

17 T. Poiger, H. –R. Buser and M. D. Mueller, *Environ. Tox. Chem.*, 20 (**2001**) 256.

18 R. M. Andreozzi, M. Rafaele and P. Nickins, *Chemosphere,* 50 (**2003**) 1319.

19 J. L. Packer, J. J. Werner, D. E. Latch, K. McNeill and W. A. Arnold, *Aquat. Sci.,* 65 (**2003**) 342.

20 C. Tixier, H. P. Singer, S. Oellers and S. R. Mueller, *Environ. Sci. Technol.,* 37 (**2003**) 1061.

21 Ciprofloxacin and Amoxicillin was a gift sample from Prof. J. Seetharamappa, Department of Chemistry, Karnataka University, Dharwad.

22 The photocatalyst Degussa P25 was a gift sample from Degussa-Huls, Frankfurt/Main, Germany.

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24 The photocatalyst TTP was obtained from Travancore Titanium Products, Kerala, India.

25 The Total Organic Carbon Analyzer was gift equipment from the Alexander von Humboldt-Stiftung, Bonn, Germany.

26 M. Muneer, J. Theurich and D. Bahnemann, *J. Photochem. Photobiol. A: Chem.*, 143 (**2001**) 213.

27 M. Muneer and D. Bahnemann, *Water Sci. Technol.*, 144 (**2001**) 331.

28 M. Muneer, H.K. Singh and D. Bahnemann, *Chemosphere*, 49 (**2002**) 193.

29 M. Atiqur Rehman, M. Muneer and D. Bahnemann, *Advan. Oxid. Technol.*, 6 (**2003**) 100.

Conclusion

The results of these studies indicate that TiO_2 can efficiently catalyze the degradation of variety of organic compounds in the presence of light. The results also indicate that degradation of the pollutant could be influenced by a number of parameters such as type of photocatalyst, pH, substrate and catalyst concentration and in the presence of electron acceptors beside molecular oxygen.

The photocatalyst, Degussa P25 was found to be more efficient for the degradation of different systems studied in this thesis. The addition of electron acceptors has not always been found to enhance the degradation rate. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain a high degradation rate, which is essential for any practical application of photocatalytic oxidation processes. The best degradation condition depends strongly on the specific kind of pollutant. The mineralization rate has been found to be slower then the decomposition rate due to the formation of intermediate products formed during the degradation process. Identification of intermediate products using GC/MS analysis technique formed during the photooxidation process were useful source of information for the degradation pathways.

List of Publications

1. Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspension of titanium dioxide

   M. M. Haque and M. Muneer

   J. Environ. Manag., 69 (**2003**) 169-176.

2. Photocatalytic degradation of a fungicide, thiram in aqueous suspension of titanium dioxide.

   M. M. Haque and M. Muneer

   Ind. J. Chem. Technol., 12 (**2005**) 68-74.

3. Photodegradation of surfactants N,N-bis(2-hydroxyethyl)dodecanoyl amide and cetyl trimethyl ammonium bromide in aqueous suspension of titanium dioxide.

   M. M. Haque and M. Muneer

   Int. J. Photoenergy, (communicated).

4. Titanium dioxide mediated photocatalyzed degradation of three selected pesticide derivatives, carbaryl, zineb and sodium diethyldithiocarbamate in aqueous suspension.

   M. M. Haque and M. Muneer

   Wat. Environ. Manag., (communicated).

5. Semiconductor mediated photocatalysed degradation of a herbicide derivative, chlorotoluron in aqueous suspension.

   M. M. Haque and M. Muneer

   Environ. Toxicol. Chem., (communicated).

6. Photocatalytic degradation of chlorbromuron in aqueous suspension of semiconductor.

   M. M. Haque and M. Muneer

   Asian. J. Environ. Poll., (communicated)

7. TiO_2-mediated photocatalytic degradation of a textile dye derivative, bromothymol blue in aqueous suspension.

   M. M. Haque and M. Muneer

   Dyes and Pigm., (communicated).

8. Photodecomposition of norfloxacin in aqueous suspension of titanium dioxide.

   M. M. Haque and M. Muneer

   Sci. Total Environ., (under preparation).

9. Photodegradation of antibiotics, ciprofloxacin and amoxicillin in aqueous suspension of titanium dioxide.

   M. M. Haque and M. Muneer

   Aquatic Sci., (under preparation).

Paper presented at conference:

Heterogeneous photocatalysed degradation of a herbicide derivatve, isoproturon in aqueous suspension of titanium dioxide under UV light and sunlight.

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89th session of Indian Science Congress, Lucknow, India January 3-7 (2002).

VITAE

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